Creating hierarchies promptly: Microwave-accelerated synthesis of ZSM-5 zeolites on macrocellular silicon carbide (SiC) foams

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HIGHLIGHTS

- Microwave-accelerated secondary growth method for synthesising ZSM-5 zeolites on SiC foams.
- Differential heating of SiC in microwave irradiation promoted the preferable growth of ZSM-5.
- Optimised conditions under microwave heating yielding ZSM-5 coatings with high specific area.
- Characterisation of ZSM-5 coatings supported on SiC foams in 3D by X-ray computed tomography.

GRAPHICAL ABSTRACT

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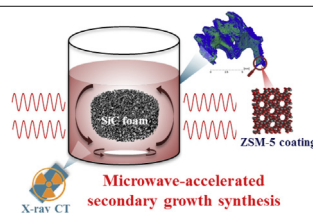
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ABSTRACT

Hierarchical ZSM-5 coatings supported on macrocellular β-SiC foams were prepared by a microwave-accelerated secondary growth method. Under microwave irradiation, differential heating was enabled due to the high microwave-adsorbing ability of SiC leading to the fast assembly of ZSM-5 zeolites on the SiC foams. The effects of crystallisation temperature, time and agitation on the growth of ZSM-5 zeolites on SiC foams were also investigated under microwave heating. A specific surface area of *ca.* 52 m^2 g^{-1} was obtained under the optimum condition of 150 °C and 4 h. Comparative studies of conventional hydrothermal and microwave-accelerated synthesis were conducted and the resulting materials were characterised extensively using XRD, SEM and N$_2$ adsorption. The combination of microwave heating, high microwave absorption of SiC substrates and agitation allowed a much more focused heating across the surface of SiC foams than conventional heating, which suppressed the formation of ZSM-5 crystals in the liquid phase and the consequent sedimentation. Additionally, for the first time, mesoscopic features of ZSM-5 coatings on SiC foam composites (>10 μm) were studied in 3D by X-ray micro computed tomography (μ-CT), providing quantitative information on the quality of the ZSM-5 coating such as the global thickness and distribution of ZSM-5 across the SiC foam supports. It was concluded that microwave-accelerated secondary growth synthesis offered an efficient route to give high quality coatings on structured foams with the good crystal quality and uniform thickness as well as lower energy consumption, especially for the substrate with a high loss tangent.

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1. Introduction

Macroscopic cellular foams, including both metallic [1–3] and ceramic [4–11], are compact structures that are easy to handle and operate with low-energy demand. They are suitable structures for developing high-throughput catalytic processes with lower energy barriers (e.g. in comparison to packed-beds [12]) and high efficiency (e.g. in comparison to monoliths [13]) due to their intricate open cell structures. Such materials are being developed with high porosity (>80%), hence high permeability, leading to low-pressure drop across the beds [12]. The stochastic nature of the interconnected cells also facilitate the axial and radial mixing by generating local eddies (even under laminar flow conditions) within the foam matrix [14], which promote the enhanced mass and momentum transfer [7,13–16]. In addition, improved heat transfer can also be achieved if the foam-based reactors are properly designed, e.g. wall coupling, enhancing the gas-phase reactions [17,18].

Silicon carbide (SiC), including both alpha (α) [4–6] and beta (β) SiC polymorphs [8,9,11,19,20], is a popular material for manufacturing macroscopic cellular foams as catalyst supports due to the intrinsic properties of SiC such as good mechanical strength, good thermal conductivity (>300 W m^{-1} K^{-1}), low thermal expansion coefficient (ca. 3×10^{-6} m m^{-1} K^{-1}) and high thermal and chemical resistance [21]. However, SiC foams have relatively low specific surface areas, i.e. <20 m^2 g^{-1}, not sufficient for promoting surface reactions in catalysis. In order to adopt SiC foams in practical settings, hierarchies must be created via surface modification to improve the specific surface area of SiC foams and enable the deposition of catalysts. Examples include: (i) the decoration of fibrous materials such as SiC nanofibres [6,22] and carbon nanotubes [23,24] via chemical vapour deposition and (ii) the coating of metal oxides such as TiO$_2$ [25,26] and zeolites such as ZSM-5 [4,5] via dip-coating or hydrothermal synthesis on the SiC surface.

Among these modifications, zeolite coatings have many advantages in catalysis [27], such as the large surface area, good mechanical strength and thermal stability [28]. In addition, their ion-exchange capacity allows a diversity of applications [19]. So far hierarchical zeolite (ZSM-5 and SAPO-34) on SiC foams have been demonstrated as being efficient for processes such as methanol dehydration to dimethyl ether [11,20] and methanol to propylene conversion [4,5].

Dip-coating and hydrothermal synthesis are two common methods for preparing hierarchical zeolite coatings on foams. Dip-coating produces a thin layer on a support based on condensation reactions between −Si−OH groups on the outer zeolite surface and hydroxyl groups on the support, but the bonding between zeolite crystals and the support is not strong. A binder is usually required to improve the interaction between zeolite crystals and support, which may block the access to the active centres leading to the deterioration in the catalytic efficiency [9,29].

Hydrothermal synthesis promotes a strong interaction between the zeolite and support due to the prolonged reaction time, normally under hydrostatic conditions [7]. Secondary growth strategies are usually employed in hydrothermal synthesis, in which nucleation and crystallisation are performed separately [30–32], to reduce the induction period. Seeding is a crucial step in a secondary growth synthesis ensuring the uniform growth of zeolite layers and the control of the crystal orientation and morphology [33]. However, the deposition phenomena under hydrothermal conditions tends to produce macroscopically uneven coatings on irregular structured configurations due to the long reaction time, where zeolite crystals are also formed in the bulk solution then precipitate due to gravity [4]. Microwave-accelerated syntheses [34,35] have been proven to be highly effective and efficient

alternatives for preparing uniformly sized zeolite crystals such as zeolite Y and ZSM-5 [34]. Microwave energy favours a change in kinetics of nucleation and crystal growth in the synthesis of zeolite leading to the relevant rate enhancements. Different thermal effects, including very high rates of temperature rise, bulk super-heating and differential heating (in non-homogeneous systems) contribute to the rapid microwave synthesis of zeolites (usually in hours) in comparison with the lengthy synthesis under conventional heating [35]. SiC ceramics have a high dielectric loss to microwave (1.71 at 2.45 GHz at 25 °C) [36] and hence can absorb electromagnetic energy and be heated rapidly and easily. Together with its high thermal effusivity and conductivity, differential heating of SiC can be achieved enabling the focused intensive heating and fast assembly of porous crystalline materials on the surface of SiC supports. Therefore, the combination of SiC substrates and microwaves can be the solution to the preparation of uniform zeolite coatings on structured SiC foams. To date, only a few studies have shown the effectiveness of microwave-assisted direct synthesis of microporous SAPO-34 zeolite on foam structures [3,11].

In this work, we report a microwave-accelerated secondary growth method to prepare hierarchical ZSM-5 zeolites on β-SiC foams. The effect of crystallisation temperature, time and agitation were investigated to establish the optimum conditions for growing uniform ZSM-5 coatings on SiC foams. Comparative studies were also performed to understand the influence of the heating methods, i.e. conventional and microwave heating, on the quality of zeolite coatings on SiC foams in terms of uniformity. Additionally, X-ray micro computed tomography was employed to allow the comprehensive characterisation of ZSM-5 coatings in 3D, especially the mesoscopic coating thickness distribution (>10 μm).

2. Experimental

2.1. Synthesis of ZSM-5 coatings on SiC foams

β-SiC foams (Fig. S1) were provided by SICAT SARL (France) and all chemicals, e.g. tetraethyl orthosilicate (TEOS, 98%), sodium aluminate (NaAlO$_2$, technical), tetramethylammonium hydroxide (TPAOH, 25% in water) and sodium chloride (NaCl, extra pure) were obtained from Fisher Scientific and used as received. The synthesis of silicalite-1 seeds was carried out by a two-step method under microwave heating [37]. The nucleation step was operated at a microwave power of 150 W and temperature of 80 °C and the crystal growth step second was continued with the same microwave power and temperature of 120 °C. The total synthesis time was about 3 h yielding silicalite-1 seeds with crystal sizes of 50–100 nm. SiC foams were calcined at 950 °C for 4 h [38] prior to the synthesis. The synthesis solution was prepared with the molar composition of TEOS: NaCl:TPAOH:NaAlO$_2$:H$_2$O = 1:0.22:0.19:0.023:178 [4] and aged at room temperature under stirring for 24 h.

ZSM-5 coatings on SiC foams were synthesised using the secondary growth method with conventional oven heating and microwave heating, respectively. The SiC foam was dip-coated with the silicalite-1 in ethanol solution (0.65 wt.%) and then dried in an oven at 160 °C. Seeded SiC foams were transferred to reactors for the secondary growth of silicalite-1 seeds into ZSM-5 crystals in the aged synthesis solution with a sodium aluminate aluminum source.

For the conventional hydrothermal synthesis, an autoclave reactor (50 mL reactor volume with 25 mL synthesis solution) was placed in an oven (Memmert UM 400, 1400 W) at 150 °C for different synthesis times to allow the growth of ZSM-5 crystals. For the microwave-assisted synthesis, a CEM Discover SP-D microwave system was used (35 mL capacity with 20 mL synthesis

solution) with an operating frequency of 2.5 GHz. The power of the microwave system was fixed at 150 W, but the synthesis temperature (110–160 °C) and time (1–5 h) were varied to investigate their effect on the crystal growth of ZSM-5. In addition, the effect of agitation (stirring at 800 rpm) under microwave conditions was also examined in the study. Blank experiments were also conducted with seed-free SiC foam in the synthesis solution and seeded SiC foam in a NaOH solution (pH = 10, simulating the same pH value of the synthesis solution), respectively. Both blank experiments were carried out at 150 °C and stirred for 4 h in the microwave system. After the synthesis, materials were washed with distilled water in an ultrasonic bath for 15 min, dried in an oven at 100 °C and calcined in a furnace with a temperature programme: from room temperature to 550 °C at a ramp rate of 1 °C min^{-1} then held at 550 °C for 4 h, to remove the template.

2.2. Characterisations of ZSM-5 coatings on SiC foam composites

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'PERT powder diffractometer using CuKα (λ = 1.5406 Å) radiation (at 30 kV and 30 mA) with a scanning rate of 2° min^{-1} in a range of from 5° to 65°. The relative crystallinity (or percent crystallinity) of zeolite ZSM-5 coating was determined by using a standard Integrated Peak Area Method [38], which involves a comparison of the integrated peak areas in the range of 22.5–25.0° 2θ. This XRD method provides the best determination of relative crystallinity when the Ref. ZSM-5 and sample ZSM-5 have a similar history of preparation and composition [39]. The calculation the relative crystallinity was performed using the Eq. (1) and the reference ZSM-5 used in this work was the ZSM-5 coating with the largest integrated peak area (i.e. under microwave heating, 150 °C, 4 h).

$$\% \text{ XRD relative crystallinity ZSM} - 5 = \frac{S_x}{S_r} \times 100 \tag{1}$$

where S_x = integrated peak area for the sample ZSM-5, and S_r = integrated peak area for the reference ZSM-5.

Scanning electron microscopy (SEM) analyses of materials were carried out using a FEI Quanta 200 ESEM in high voltage mode of 20 kV. Platinum coating of samples was performed using an Emitech K550X sputter coater under vacuum conditions of 1×10^{-4} mbar. Nitrogen adsorption/desorption isotherms of materials at -196 °C were measured by using a Micromeritics ASAP 2020 analyser and the surface areas were calculated based on Brunauer–Emmett–Teller (BET) theory. Materials were degassed at 100 °C for 12 h prior to the nitrogen adsorption.

2.3. X-ray micro computed tomography (μ-CT) of ZSM-5 coatings on SiC foam composites

A ZEISS X-ray CT scanner (ZEISS Xradia 520 Versa, USA) was used in this study to generate radiographs of the composite materials using the scanning parameters as in Table S1. This particular scanner has a number of magnification optics to increase the resolution for a fixed source/detector distance, and in this case the standard 0.4× objective was used. The detector consists of 2048 × 2048 pixels, each 13 μm in size, which when coupled with the 0.4× objective and the geometric magnification of 6× resulted in an image pixel size of 4.45 μm. The radiographs from the scan were reconstructed using ZEISS proprietary software that employs a filtered back projection algorithm [40,41], exporting the volume as a DICOM image stack. This was then reconstructed as the three-dimensional (3D) model in Avizo (FEI, version 8, USA) for segmentation and visualisation.

3. Results and discussion

3.1. Calcination of SiC foams and seeding

After calcination in air, the formation of a thin SiO$_2$ layer on the surface of SiC substrate was detected [19,20,38,42]. The oxidative conversion of surface SiC substrate to the thin SiO$_2$ layer was indicated by weight gain of SiC foams after calcination (by ca. 20%), considering the stoichiometry of SiC oxidation (Eq. (2)) [42]. As seen in Fig. 1, SEM images of SiC substrate clearly showed the change of the surface morphology before (Fig. 1a) and after (Fig. 1b) the calcination. XRD diffractograms of materials in Fig. 1a and b are presented in Fig. 1c. XRD results (Fig. 1c) showed the appearance of a broad peak after calcination, located approximately at 2θ = 21.7°, which is the characteristic diffraction pattern of the amorphous SiO$_2$ phase (JCPDS data, card No. 01–086-1561 [43]).

$$SiC(s) + \frac{3}{2} O_2(g) \rightarrow SiO_2(s) + CO(g) \tag{2}$$
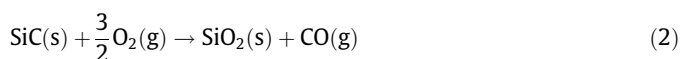
The presence of the thin SiO$_2$ layer ensures a strong interaction between the support and the seed gel [19,20]. The surface SiO$_2$ has intrinsic hydroxyl groups (silanols) in an aqueous solution [44]. Silicalite-1 is the pure silicon form of ZSM-5 also with $-$Si$-$OH groups protruding from the surface. Therefore, the dehydration of adjacent silanols from the SiO$_2$ layer and silicalite-1 seeds [45], which results from the physisorption of silicalite-1 seeds on the substrate, leads to the formation of siloxanes with strong Si$-$O bonds. As shown in Fig. S2, silicalite-1 seeds were uniformly anchored on the surface of a SiC foam after seeding and the weight gain from the seeding was measured as ca. 0.65%. The seeded SiC foam was dried at 160 °C overnight to further enhance the anchorage silicalite-1 seeds on the surface of SiC foams [46]. To test the anchorage between silicalite-1 seeds and the calcined SiC foams, seeded samples were immersed in a NaOH solution (pH = 10, simulating the pH value of the synthesis solution in the secondary growth method) and treated at 150 °C for 4 h under microwave irradiation. After the treatment, silicalite-1 seeds were found to be still attached to the surface of SiC foams shown by SEM analyses (Fig. S2).

Blank experiments using the calcined SiC and seeded SiC foams were carried out in the synthesis solution (TEOS:NaCl:TPAOH: NaAlO$_2$:H$_2$O = 1:0.22:0.19:0.023:178) to examine the effectiveness of the secondary growth method. It was found that, under the
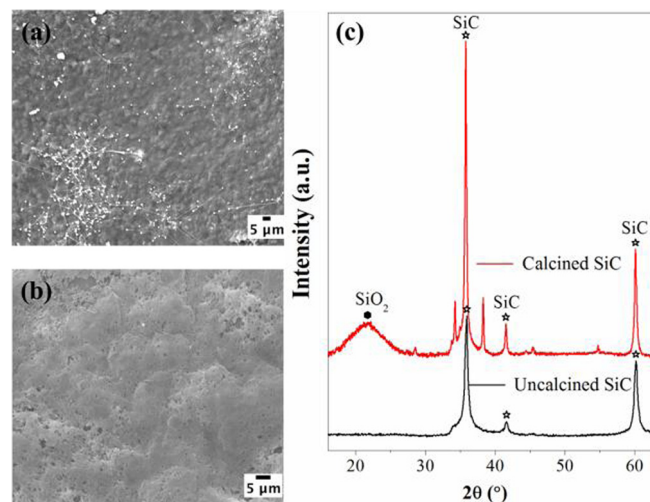

Fig. 1. Surface morphology of β–SiC foams by SEM: (a) before calcination and (b) after calcination; and (c) XRD patterns of fresh and calcined β–SiC substrate.

conditions used (microwave heating, 150 °C, 4 h), silicalite-1 seeds are crucial to allow the synthesis of ZSM-5 coatings on SiC substrate (Fig. S2). Only *ca.* 2.4 wt.% ZSM-5 coatings were produced on the surface of SiC foams with unseeded substrate, while a well-developed layer of 8 wt.% ZSM-5 zeolite was formed on the SiC foam with the seeded sample.

3.2. Microwave-assisted syntheses of ZSM-5 coatings on SiC foams

Temperature is a key parameter in controlling nucleation and the crystallisation rate, and hence the crystallinity, morphology and purity of the synthesised ZSM-5 zeolite [47,48]. In this work, the temperature effect on the secondary growth of ZSM-5 crystals on SiC foams was studied under microwave heating. Experiments were performed by varying crystallisation temperature (110 °C to 160 °C in 10 °C increments) at a constant seed concentration (0.65 wt.%), synthesis gel composition and synthesis time (3 h).

XRD patterns of materials (Fig. 2) prepared at different temperatures under stirring confirmed the presence of the zeolite ZSM-5 phase in the sample with the doublets in a 2θ range of 23.1 and 23.8° corresponding to the peaks of 501 and 303 crystal surface [49]. For the XRD peak at around 24.5° 2θ, a singlet was noticed for the samples suggesting the formation of the orthorhombic crystalline form under the conditions used for the preparation of ZSM-5 coating [39]. As seen in Fig. 2, the intensity of peaks of 501 and 303 crystal surface increased with an increase of crystallisation temperature under microwave irradiation. It was reported that, the nucleation rate decreases and the crystallisation rate increases remarkably by increasing the synthesis temperature (under hydrothermal conditions with TPAOH as the template), leading to a huge difference in ZSM-5 crystallinity (*ca.* 40%) [47]. In this work, the integrated peak area method [39] was used to determine the relative crystallinity of ZSM-5 coatings, which is shown in Table 1. Under stirring at 800 rpm and at a constant synthesis time of 3 h,
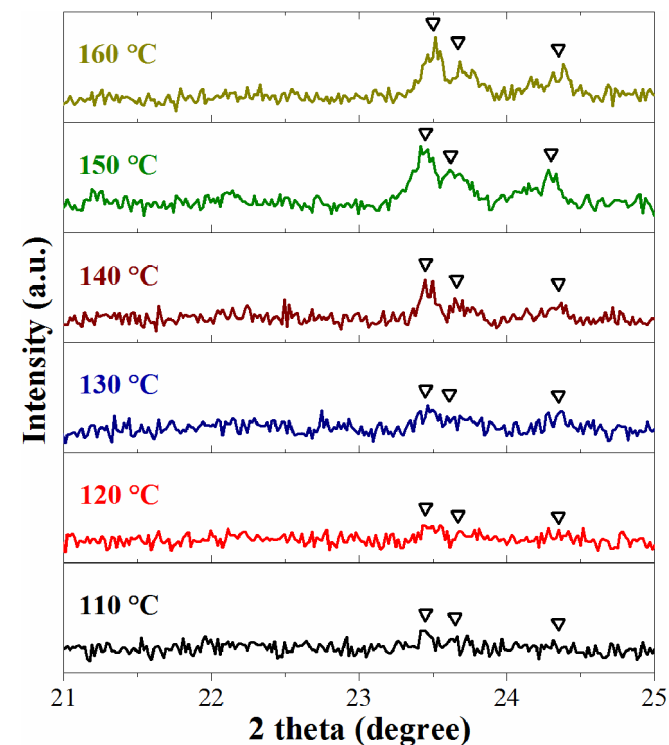
the relative crystallinity of ZSM-5 coatings on SiC foams increased with an increase of the crystallisation temperature and peaked at 150 °C with a value of 92.6%. The same trend was also found for their specific surface areas.

Under conventional heating, crystallisation temperature strongly influenced the crystallinity of ZSM-5 zeolites [48,50]. To prepare ZSM-5 zeolite in its bulk form, high temperatures at >150 °C were usually needed to ensure good relative crystallinities [48,50,51]. SiC is a strong microwave absorber with high thermal effusivity, which can absorb microwaves and produce higher local surface temperatures than that of bulk fluid facilitating the fast growth of ZSM-5 zeolites on SiC surfaces. In this work, a relative crystallinity of ZSM-5 coating was achieved as 92.6% at 150 °C over 3 h, while similar result can only be achieved with >20 h crystallisation time under conventional heating at 150 °C [48,50].

SEM analysis of resulting materials (Fig. 3) showed the morphology of ZSM-5 coatings on SiC substrates. ZSM-5 zeolite crystals tended to aggregate with the neighbouring ones and self-assembled into intergrown and interlocking crystals forming dense and continuous layers on the surface of SiC foams. Both the morphology and crystal size of the surface ZSM-5 were found to change along with an increase of synthesis temperature under microwave heating, *i.e.* (i) shape from spherulite to euhedral and (ii) size from nanometers to microns (Table 1). At 150 °C, ZSM-5 coatings with the orthorhombic-shaped crystals with average size of about 3 μm were obtained (Fig. 3b).

Agitation is crucial in the microwave-accelerated synthesis of ZSM-5 coatings on SiC foams (Table 1). This can be attributed to the homogenisation of species and temperatures of the synthesis solution promoted by the stirring. Under hydrostatic conditions with microwave heating, the temperature window of producing quality ZSM-5 coatings was 130–150 °C. Only the amorphous phase was obtained at 120 °C and, at 160 °C, cracks were found in the ZSM-5 layer (Fig. 4), which can be ascribed to the different thermal expansion behaviors of the SiC substrate and ZSM-5 coatings [52,53] (see Fig. 4).

The growth time is also a major factor in the secondary growth of zeolites [48,50,51]. To examine the effect of this parameter, experiments were conducted at 150 °C with different crystallisation times under stirring and microwave heating. XRD analyses (Fig. 5) showed that ZSM-5 crystalline phase was formed even within one hour using the secondary growth method with microwave heating. Relative crystallinity and specific surface area at different crystallisation times are summarised in Table 1. By increasing the crystallisation time from 1 to 4 h at 150 °C, relative crystallinity increased by 60%, which can be ascribed to the ongoing crystallisation of ZSM-5 phase. The highest relative crystallinity was obtained for the sample synthesised at 4 h under microwave heating. The measured specific surface area of materials is compatible with the result of the relative crystallinity (N_2 adsorption-desorption isotherms are shown in Fig. S3).

The morphology of ZSM-5 on SiC foams prepared over different growth times is shown in Fig. 6. It was found that, under microwave heating, ZSM-5 zeolite coatings prepared in one hour mainly had spherulite shapes (Fig. 6a). With crystallisation times longer than two hours, twinned and intergrown ZSM-5 crystals with smooth surfaces and euhedral shapes were formed (Fig. 5b and c). The average particle size also increased gradually as a function of synthesis time and an average particle size of 3 μm was obtained after four hours (Fig. 6c).

After studying different parameters under microwave heating, we arrived at an optimum condition of 150 °C over four hours with stirring producing ZSM-5 coatings on SiC foams with a good crystallinity and specific surface area (*ca.* 52 $m^2 \, g^{-1}$). In addition, the mechanical bond of ZSM-5 coatings on the host structure was examined for the composite structures prepared at 150 °C (4 h).

Fig. 2. XRD short scan patterns of zeolite ZSM-5 coatings (calcined) on SiC foams prepared at different temperatures under microwave heating (amorphous SiO_2 diffraction peaks were subtracted from the XRD patterns).

Table 1
Microwave-assisted synthesis conditions of ZSM-5 coatings on SiC foams and parameters of specific surface area[1] and relative crystallinity of the synthesised ZSM-5 coatings.

Temperature (°C)	Time (h)	Stirring (–)	BET area (m² g⁻¹)[2]	Relative crystallinity (%)[3]	Crystal size (μm)	Crystal shape (–)
110	3	Yes	17.6	20.1	0.27–0.33	Spherulite
120	3	Yes	19.8	24.0	0.34–0.40	Spherulite
130	3	Yes	21.2	35.4	0.60–0.80	Spherulite
140	3	Yes	26.3	37.1	0.60–0.80	Spherulite
150	3	Yes	38.4	92.6	1.8–2.5	Euhedral
160	3	Yes	37.9	74.7	2.2–2.9	Euhedral
120	3	No	Not measured	0	Not measured	Not measured
150	3	No	34.3	41.3	1.0–1.3	Spherulite
150	1	Yes	23.4	40.0	0.45–0.50	Spherulite
150	2	Yes	26.5	51.1	0.70–0.90	Spherulite
150	4	Yes	52.1	100	2.5–3.0	Euhedral

[1] Intrinsic BET surface areas of original SiC foam and calcined SiC foam are 17.3 and 13.3 m² g⁻¹, respectively.
[2] Values are overall BET areas of ZSM-5 on SiC foam campsites.
[3] Margin of errors of relative crystallinity is <5%.
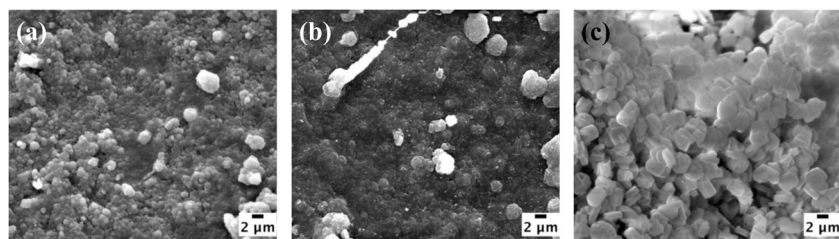
Fig. 3. SEM micrographs of ZSM-5 coatings (calcined) on SiC foams prepared under stirring over 3 h at (a) 110 °C, (b) 130 °C and (c) 150 °C.
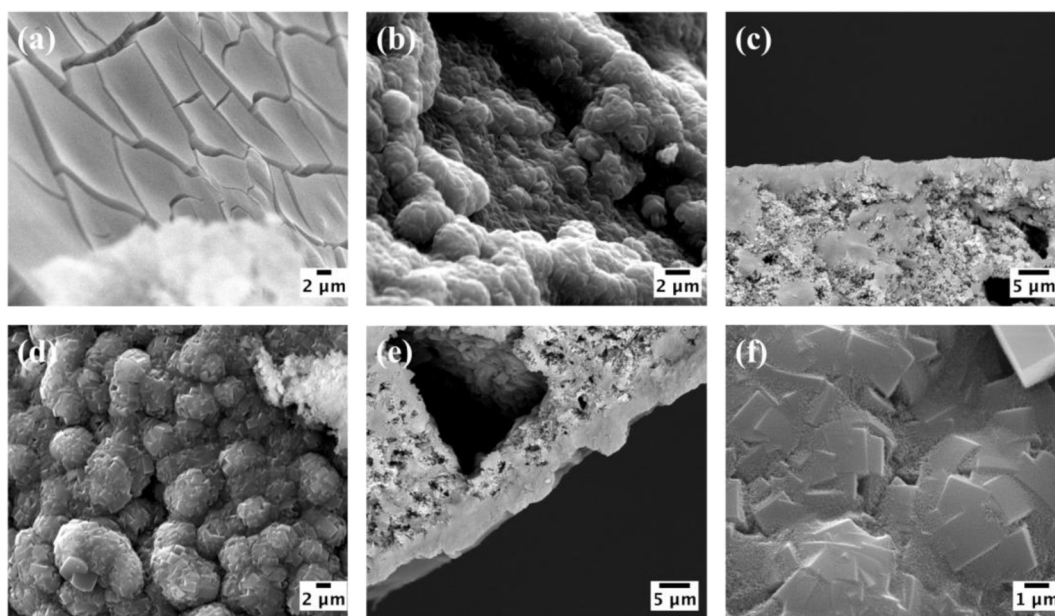
Fig. 4. SEM micrographs of ZSM-5 coating on SiC foams prepared under hydrostatic conditions and microwave irradiation at various: crystallisation temperatures: (a) 120 °C; (b) and (c) (cross section of the composite) 130 °C; (d) and (e) (cross section of the composite) 150 °C; (f) 160 °C.

After ultrasonic treatment of 45 min in water, only 0.45% weight loss was measured showing the robustness of the developed materials.

3.3. Secondary growth synthesis under conventional and microwave heating

In order to demonstrate the effectiveness of the microwave heating for promoting the crystal growth on SiC surfaces, a comparative study of microwave-assisted and conventional hydrothermal synthesis of ZSM-5 coatings on SiC foams was carried out. XRD analyses (Fig. 7a) showed that both heating methods were able to grow ZSM-5 zeolites on SiC foams by secondary growth synthesis under similar conditions (i.e. same seed concentration and synthesis solution composition, T = 150 °C, t = 4 h). Due to the focused heating on the SiC surface under the microwave irradiation, a better crystallinity of ZSM-5 coating was produced in comparison with that from conventional heating (Fig. S4). N₂ adsorption isotherms of materials are shown in Fig. 7b. For all materials, clear two-step increases in the amount of nitrogen
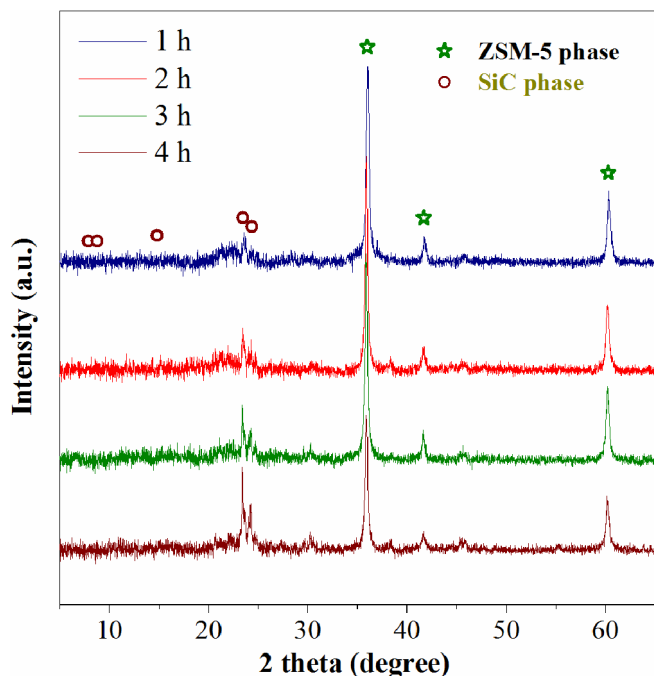
Fig. 5. XRD patterns of zeolite ZSM-5 coatings (calcined) on SiC foams prepared at 150 °C over different synthesis time (amorphous SiO_2 diffraction peaks were subtracted from the XRD patterns).

ZSM-5 coatings, isotherms showed the linear increase in the nitrogen uptake at low relative pressures ($p/p^0 < 0.05$) indicating the increase of micropores in the composite materials. The calculated BET surface areas of the composite materials prepared by conventional and microwave heating were $30.0\ m^2\ g^{-1}$ (Fig. S5) and $52.1\ m^2\ g^{-1}$, respectively, showing that the microwave heating is more effective than the conventional heating for promoting the ZSM-5 crystal growth on SiC surface.

After 4 h at 150 °C, about 3.6 wt.% weight gain was obtained by the conventional heating, whereas *ca.* 8 wt.% of ZSM-5 was promoted by the microwave heating. To achieve a similar weight gain of *ca.* 10 wt.%, 48 h of growth time was needed in the conventional hydrothermal synthesis. Considering the comparable ZSM-5 loading on SiC foams, the bulk appearance of ZSM-5 coatings on SiC foams prepared by the two heating methods was distinct, as seen in Fig. S6. Apart from the microscopic (<10 μm) dense coating that was visualised by SEM (Fig. S7), macroscopic ZSM-5 sediments as well as bare SiC surfaces were found for materials prepared by the conventional hydrothermal synthesis under hydrostatic conditions (Fig. S6a). On the other hand, microwave-assisted synthesis yielded a continuous and uniform layer of ZSM-5 zeolites across SiC foams (Fig. S6b).

The conventional hydrothermal synthesis was carried out in an autoclave reactor, where both the liquid bulk and the SiC support were heated evenly, leading to the crystallisation both in the liquid bulk and on the SiC surface with similar kinetics. A blank experiment was carried out under conventional heating ($T = 150$ °C) with the synthesis solution only without the SiC substrate. It was found that nucleation and crystallisation were also possible in the liquid bulk yielding ZSM-5 crystals. Therefore, the phenomenon of sedimentation during the conventional synthesis inevitably caused the uneven deposition of ZSM-5 zeolite on the surface of SiC foams
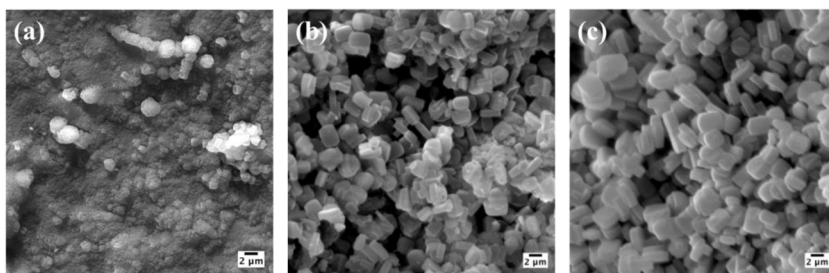
uptake were found over the whole relative pressure range (type IV adsorption isotherms) suggesting the presence of micro-/mesopores. By creating hierarchies on SiC foams with microporous

Fig. 6. SEM images of ZSM-5 coatings (calcined) on SiC foams prepared under stirring at 150 °C over (a) 1 h, (b) 2 h and (c) 4 h.
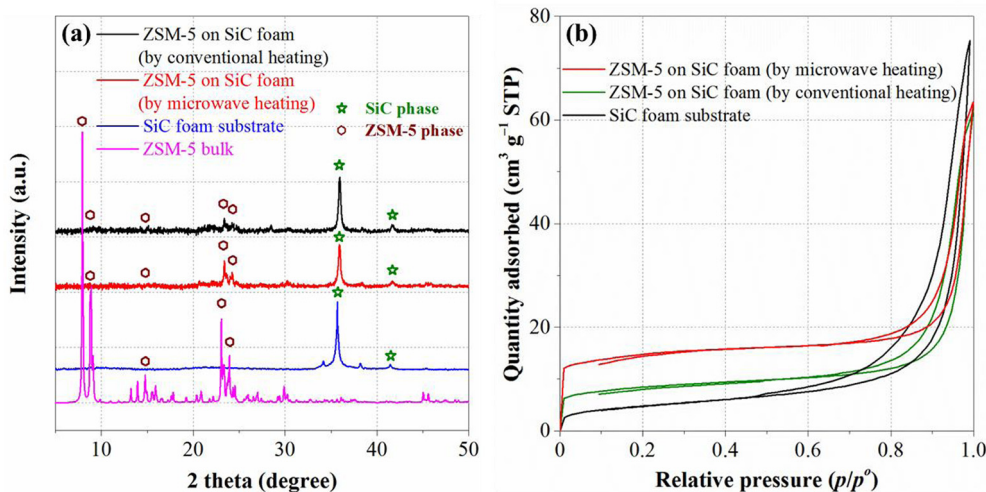

Fig. 7. (a) XRD patterns and (b) N_2 adsorption-desorption isotherms of ZSM-5 coatings on SiC foam composites prepared by different heating methods ($T = 150$ °C, $t = 4$ h).

(Fig. S6a), *i.e.* due to gravity under the hydrostatic conditions, the ZSM-5 crystals formed in the liquid phase would precipitate onto the upward facing surface of SiC foams. Additionally, this phenomena was found more profoundly with a synthesis time longer than 12 h.

Under microwave irradiation, differential heating was enabled in the present system due to the big difference in the loss tangent (δ, the ability of a material to convert microwave energy into heat [54]) between the liquid bulk (mainly water, δ_{water} = 0.16 [54]) and SiC substrate (δ_{SiC} = 1.71 [36]). Therefore, SiC supports absorbed microwaves more efficiently than the aqueous synthesis solution and produced the effective heating across the surface of SiC foams, resulting in the preferable fast synthesis of ZSM-5 zeolites on SiC foams. Furthermore, with the stirring, the species in the liquid bulk were homogenised and the contact between species and nucleates on SiC surfaces was encouraged. By combining the high thermal energy on the SiC surface, species were quickly consumed for

assembling ZSM-5 framework on SiC surfaces suppressing the nucleation and crystallisation in the liquid phase.

Routine SEM characterisation of materials can only provide the local microscopic information of the developed materials, such as the local thickness of dense layers of ZSM-5 coatings on the surface of SiC foams (Fig. S8). In order to characterise of the global uniformity of ZSM-5 coatings on SiC foams quantitatively, non-destructive X-ray micro computed tomography (μ-CT) was performed. The images obtained from the CT scan, as seen in Fig. 8, showed the two-dimensional slices (radiographs) of materials. It was found that ZSM-5 and SiC attenuated x-rays differently yielding different greyscales (Table S2), which enabled the quantitative segmentation of CT radiographs.

Avizo 8 (FEI, USA) was used for visualisation and quantification of the composite structures. The ZSM-5 coating occupied a distinct range of grey-values compared to the SiC struts (and against the background/pores, as seen in Table S2) enabling segmentation such that the material dimension parameters could be extracted. Segmentation was performed using a watershed thresholding method [55] to separate the background/pore, SiC strut and ZSM-5 coating regions. This segmentation method is analogous to the flood filling of a topographical map where the height is equivalent to the grey value intensity. From initial markers of the individual phase the algorithm allows a gradient dependent flood filling of the map, where the gradient magnitude of grey value in the flooding direction is relatively high the filling is slower, and conversely where this gradient is relatively low the filling is faster. The volumes contained three distinct phases, *i.e.* pores, zeolite coatings and SiC struts that were assigned initial threshold markers of grey values respectively (Table S2). From these basins the watershed algorithm filled the rest of the volume for each of the phases simultaneously, resulting in the segmentation to be analysed.

The distribution of ZSM-5 coatings on the surfaces of SiC foams are exemplified in Fig. 9, ZSM-5 coatings as the yellow rendering and the SiC substrate as the purple (in the sample prepared by conventional heating) and blue (in the sample prepared by microwave heating) renderings. The 3D models provide a holistic view into the overall coating quality of materials developed by the conventional and microwave heating. As seen in Fig. 9a, large amount of ZSM-5
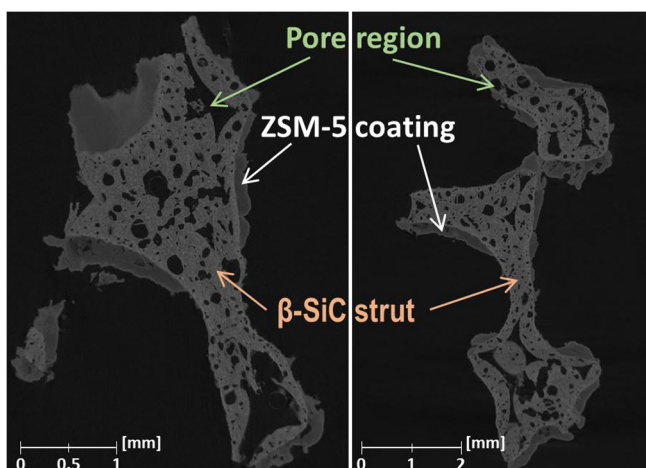

Fig. 8. Orthoslices of ZSM-5 coatings on SiC foam composites, indicating μ-CT is an efficient characterisation tool for evaluating composite materials.
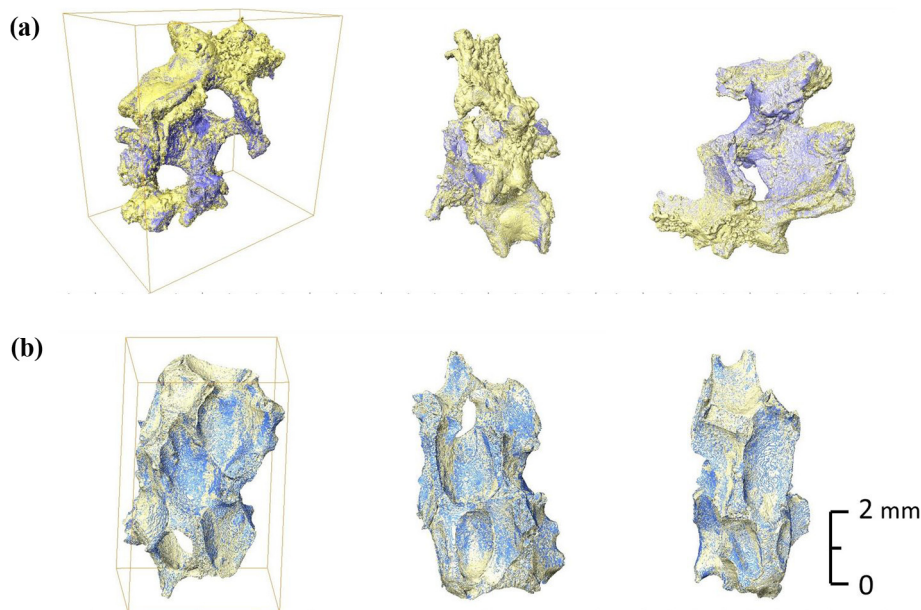

Fig. 9. 3D rendering of μ-CT data of ZSM-5 coatings (>10 μm thickness) on SiC foam composites prepared by (a) conventional heating (T = 150 °C, t = 48 h, 10 wt.% zeolite coating) and (b) microwave heating (T = 150 °C, t = 4 h, 8 wt.% zeolite coating).

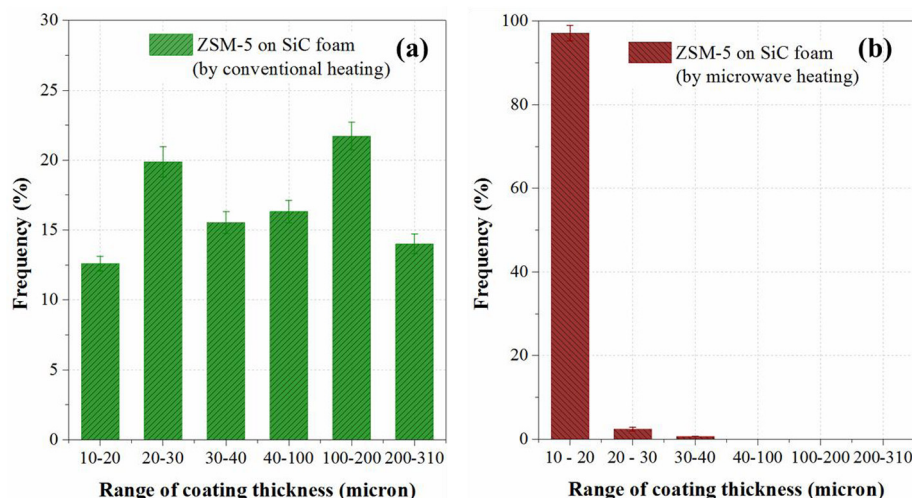**Fig. 10.** Mesoscopic ZSM-5 coating thickness distribution determined by μ-CT characterisation (>10 μm): (a) ZSM-5 on SiC foam synthesised by the conventional heating (T = 150 °C, t = 48 h, 10 wt.% zeolite coating) and (b) ZSM-5 on SiC foam synthesised by the microwave heating (T = 150 °C, t = 4 h, 8 wt.% zeolite coating).

phase is evident on the upward facing surface of the SiC support evidencing the effect of sedimentation during hydrothermal synthesis. However, it is noticeable that the appearance of ZSM-5 coatings by the microwave-accelerated synthesis is much more uniform than that in the conventional heating.

The quantification of the thickness distribution of ZSM-5 coatings (above 10 μm) was extracted and shown in Fig. 10. The thickness distribution of ZSM-5 coatings from the conventional heating is much wider than that from the microwave heating. For the sample prepared by the conventional heating, the coating thickness distribution measured by μ-CT was wide from 10 to 308 μm (Fig. 10a). About 36% of the ZSM-5 coating has the thickness of >100 μm evidencing the precipitation phenomenon under conventional heating. For the sample prepared by the microwave heating, as seen in Fig. 10b, the thickness distribution was very narrow with a major distribution (97%) between 10 and 20 μm and the thickest coating of 30.4 μm. This comparison provided proof of a superior coating uniformity promoted by the microwave heating than that of conventional heating. Considering the energy consumption of the two synthesis methods, microwave accelerated method was much more energy efficient than the conventional hydrothermal synthesis, i.e. about 20,000 kJ g zeolite^{-1} for the conventional heating versus about 1200 kJ g zeolite^{-1} for the microwave heating.

4. Conclusions

The microwave-accelerated secondary growth method has been demonstrated to be highly effective to synthesise uniform ZSM-5 coating on SiC foams. At a constant seed concentration and synthesis gel composition, the effects of agitation, crystallisation time and temperature on the crystallinity, morphology and specific surface area of the resulting ZSM-5 zeolite on SiC foam composites were investigated. The optimum condition was established as: 150 °C for 4 h, resulting in a 8 wt.% ZSM-5 coating on the SiC foam with the excellent uniformity and a specific surface area of ca. 52 m^2 g^{-1}.

A comparative study was conducted to understand the influence of heating methods, i.e. conventional and microwave heating, on the coating quality. It was found that the deposition of ZSM-5 crystals on the upward facing surface of SiC foams played an important role in the formation of coating layer under conventional heating and hydrostatic conditions. On the contrary, the differential heating phenomenon was observed when SiC supports

were irradiated by microwave, which allowed a very focused heating across the surface of SiC foams leading to a fast and homogeneous ZSM-5 crystal growth on the surface of SiC foams. Agitation was believed to be able to homogenise the species dispersion in the liquid bulk and enhance the contact between species and nuclei on SiC surfaces preventing the nucleation and crystallisation in the liquid phase.

X-ray micro computed tomography (μ-CT) was employed for the first time to characterise the mesoscopic zeolite (>10 μm) on SiC foam composite materials. μ-CT imaging is an effective tool to obtain the digitised rendering of real composite materials based on foams and extract the mesoscopic features of ZSM-5 coatings. The obtained 3D models provided the complementary information of the hierarchical structure of the developed composite materials. In association with the conventional SEM analysis, the accurate determination of coating thickness was achieved. It was found that the developed microwave-assisted secondary growth synthesis was an effective method to prepare ZSM-5 coating on SiC foams with the uniform coating thickness, i.e. thickness distribution of 10–20 μm. In contrast, a wide distribution of coating thickness (10–300 μm) was promoted by the conventional hydrothermal synthesis mainly due to the sedimentation phenomenon. To conclude, the combination of microwave heating and SiC substrate offers a rapid route to yield quality ZSM-5 coating on SiC foams with good crystallinity and uniform thickness, as well as less energy consumption.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.11.116.

References

[1] E. Bianchi, T. Heidig, C.G. Visconti, G. Groppi, H. Freund, E. Tronconi, An appraisal of the heat transfer properties of metallic open-cell foams for strongly exo-/endo-thermic catalytic processes in tubular reactors, Chem. Eng. J. 198 (2012) 512–528.

[2] E. Tronconi, G. Groppi, C.G. Visconti, Structured catalysts for non-adiabatic applications, Curr. Opin. Chem. Eng. 5 (2014) 55–67.

[3] L. Bonaccorsi, L. Calabrese, A. Freni, E. Proverbio, Hydrothermal and microwave synthesis of SAPO (CHA) zeolites on aluminium foams for heat pumping applications, Microporous Mesoporous Mater. 167 (2013) 30–37.

[4] Y. Jiao, C. Jiang, Z. Yang, J. Zhang, Controllable synthesis of ZSM-5 coatings on SiC foam support for MTP application, Microporous Mesoporous Mater. 162 (2012) 152–158.

[5] Y. Jiao, C. Jiang, Z. Yang, J. Liu, J. Zhang, Synthesis of highly accessible ZSM-5 coatings on SiC foam support for MTP reaction, Microporous Mesoporous Mater. 181 (2013) 201–207.

[6] Y. Jiao, X. Yang, C. Jiang, C. Tian, Z. Yang, J. Zhang, Hierarchical ZSM-5/SiC nano-whisker/SiC foam composites: preparation and application in MTP reactions, J. Catal. 332 (2015) 70–76.

[7] F.C. Buciuman, B. Kraushaar-Czarnetzki, Preparation and characterization of ceramic foam supported nanocrystalline zeolite catalysts, Catal. Today 69 (2001) 337–342.

[8] S. Ivanova, E. Vanhaecke, B. Louis, S. Libs, M.J. Ledoux, S. Rigolet, C. Marichal, C. Pham, F. Luck, C. Pham-Huu, Efficient synthesis of dimethyl ether over HZSM-5 supported on medium-surface-area beta-SiC foam, ChemSusChem 1 (2008) 851–857.

[9] S. Ivanova, C. Lebrun, E. Vanhaecke, C. Pham-Huu, B. Louis, Influence of the zeolite synthesis route on its catalytic properties in the methanol to olefin reaction, J. Catal. 265 (2009) 1–7.

[10] C. Duong-Viet, H. Ba, Z. El-Berrichi, J.M. Nhut, M.J. Ledoux, Y.F. Liu, C. Pham-Huu, Silicon carbide foam as a porous support platform for catalytic applications, New J. Chem. 40 (2016) 4285–4299.

[11] M.M. Elamin, O. Muraza, Z. Malaibari, H. Ba, J.-M. Nhut, C. Pham-Huu, Microwave assisted growth of SAPO-34 on β-SiC foams for methanol dehydration to dimethyl ether, Chem. Eng. J. 274 (2015) 113–122.

[12] M. Lacroix, P. Nguyen, D. Schweich, C. Pham Huu, S. Savin-Poncet, D. Edouard, Pressure drop measurements and modeling on SiC foams, Chem. Eng. Sci. 62 (2007) 3259–3267.

[13] R.R. Zapico, P. Marín, F.V. Díez, S. Ordóñez, Liquid hold-up and gas–liquid mass transfer in an alumina open-cell foam, Chem. Eng. Sci. 143 (2016) 297–304.

[14] X. Fan, X. Ou, F. Xing, G.A. Turley, P. Denissenko, M.A. Williams, N. Batail, C. Pham, A.A. Lapkin, Microtomography-based numerical simulations of heat transfer and fluid flow through β-SiC open-cell foams for catalysis, Catal. Today 278 (2016) 350–360.

[15] H. Li, F.Z. Wang, C.C. Wang, X. Gao, X.G. Li, Liquid flow behavior study in SiC foam corrugated sheet using a novel ultraviolet fluorescence technique coupled with CFD simulation, Chem. Eng. Sci. 123 (2015) 341–349.

[16] X. Ou, X. Zhang, T. Lowe, R. Blanc, M.N. Rad, Y. Wang, N. Batail, C. Pham, N Shokri, A. Garforth, P. Withers, X. Fan, X-ray microtomography characterization of cellular SiC foams for their applications in chemical engineering, Mater. Charact. 123 (2017) 20–28, http://dx.doi.org/10.1016/j.matchar.2016.11.013.

[17] S. Razza, T. Heidig, E. Bianchi, G. Groppi, W. Schwieger, E. Tronconi, H. Freund, Heat transfer performance of structured catalytic reactors packed with metal foam supports: influence of wall coupling, Catal. Today 273 (2016) 187–195.

[18] E. Bianchi, G. Groppi, W. Schwieger, E. Tronconi, H. Freund, Numerical simulation of heat transfer in the near-wall region of tubular reactors packed with metal open-cell foams, Chem. Eng. J. 264 (2015) 268–279.

[19] B.L.S. Ivanova, B. Madani, J.P. Tessonnier, M.J. Ledoux, C. Pham-Huu, ZSM-5 Coatings on β-SiC monoliths: possible new structured catalyst for the methanol-to-olefins process, J. Phys. Chem. C 111 (2007) 4368–4374.

[20] Y. Liu, S. Podila, D.L. Nguyen, D. Edouard, P. Nguyen, C. Pham, M.J. Ledoux, C. Pham-Huu, Methanol dehydration to dimethyl ether in a platelet milli-reactor filled with H-ZSM5/SiC foam catalyst, Appl. Catal. A 409–410 (2011) 113–121.

[21] T.W. Wong, Handbook of Zeolites: Structure, Nova Science Publishers, New York, United States, Properties and Applications, 2009.

[22] D. Edouard, S. Ivanova, M. Lacroix, E. Vanhaecke, C. Pham, C. Pham-Huu, Pressure drop measurements and hydrodynamic model description of SiC foam composites decorated with SiC nanofiber, Catal. Today 141 (2009) 403–408.

[23] H. Yuan, H. Liu, B. Zhang, L. Zhang, H. Wang, D.S. Su, A Pd/CNT-SiC monolith as a robust catalyst for Suzuki coupling reactions, Phys. Chem. Chem. Phys. 16 (2014) 11178–11181.

[24] L. Truong-Phuoc, T.H. Tri, N.D. Lam, W. Baaziz, T. Romero, D. Edouard, D. Begin, I. Janowska, C. Pham-Huu, Silicon carbide foam decorated with carbon nanofibers as catalytic stirrer in liquid-phase hydrogenation reactions, Appl. Catal. A 469 (2014) 81–88.

[25] N.A. Kouamé, D. Robert, V. Keller, N. Keller, C. Pham, P. Nguyen, Preliminary study of the use of β-SiC foam as a photocatalytic support for water treatment, Catal. Today 161 (2011) 3–7.

[26] N.A. Kouame, D. Robert, V. Keller, N. Keller, C. Pham, P. Nguyen, TiO₂/beta-SiC foam-structured photoreactor for continuous wastewater treatment, Environ. Sci. Pollut. Res. Int. 19 (2012) 3727–3734.

[27] W. Schwieger, A.G. Machoke, T. Weissenberger, A. Inayat, T. Selvam, M. Klumpp, A. Inayat, Hierarchy concepts: classification and preparation strategies for zeolite containing materials with hierarchical porosity, Chem. Soc. Rev. 45 (2016) 3353–3376.

[28] A. Corma, State of the art and future challenges of zeolites as catalysts, J. Catal. 216 (2003) 298–312.

[29] O. Leonard, Zeolite coatings applied in structured catalyst packings, in, 1998.

[30] S. Mintova, J. Hedlund, B. Schoeman, V. Valtchev, J. Sterte, Continuous films of zeolite ZSM-5 on modified gold surfaces, Chem. Comm. 15–16 (1997).

[31] Y. Yan, S.S. Jiang, H.P. Zhang, X.Y. Zhang, Preparation of novel Fe-ZSM-5 zeolite membrane catalysts for catalytic wet peroxide oxidation of phenol in a membrane reactor, Chem. Eng. J. 259 (2015) 243–251.

[32] H. Chen, H. Zhang, Y. Yan, Preparation and characterization of a novel gradient porous ZSM-5 zeolite membrane/PSSF composite and its application for toluene adsorption, Chem. Eng. J. 209 (2012) 372–378.

[33] F. Qiu, X. Wang, X. Zhang, H. Liu, S. Liu, K.L. Yeung, Preparation and properties of TS-1 zeolite and film using Sil-1 nanoparticles as seeds, Chem. Eng. J. 147 (2009) 316–322.

[34] A. Arafat, J.C. Jansen, A.R. Ebaid, H. Vanbekkum, Microwave preparation of zeolite-y and ZSM-5, Zeolites 13 (1993) 162–165.

[35] C.S. Cundy, Microwave techniques in the synthesis and modification of zeolite catalysts. A review, Collect. Czech. Chem. Commun. 63 (1998) 1699–1723.

[36] G. Zou, M. Cao, H. Lin, H. Jin, Y. Kang, Y. Chen, Nickel layer deposition on SiC nanoparticles by simple electroless plating and its dielectric behaviors, Powder Technol. 168 (2006) 84–88.

[37] J. Motuzas, A. Julbe, R.D. Noble, C. Guizard, Z.J. Beresnevicius, D. Cot, Rapid synthesis of silicalite-1 seeds by microwave assisted hydrothermal treatment, Microporous Mesoporous Mater. 80 (2005) 73–83.

[38] G. Wine, J.P. Tessonnier, S. Rigolet, C. Marichal, M.J. Ledoux, C. Pharn-Huu, Beta zeolite supported on a beta-SiC foam monolith: a diffusionless catalyst for fixed-bed Friedel-Crafts reactions, J. Mol. Catal. A 248 (2006) 113–120.

[39] Standard test method for determination of relative crystallinity of zeolite ZSM-5 by X-ray diffraction, ASTM International, West Conshohocken, United States, 2011.

[40] A.C. Kak, M. Slaney, Principles of Computerized Tomographic Imaging, Society for Industrial and Applied Mathematics, Philadelphia, United States, 1988.

[41] F. Natterer, F. Wübbeling, Mathematical Methods in Image Reconstruction, Society for Industrial and Applied Mathematics, Philadelphia, United States, 2001.

[42] R. Moene, M. Makkee, J.A. Moulijin, High surface area silicon carbide as catalyst support characterization and stability, Appl. Catal. A 167 (1998) 321–330.

[43] C.S. Ferreira, P.L. Santos, J.A. Bonacin, R.R. Passos, L.A. Pocrifka, Rice husk reuse in the preparation of SnO₂/SiO₂ nanocomposite, Mater. Res. 18 (2015) 639–643.

[44] Q. Xu, Materials engineering and environmental science, Proceedings of the 2015 International Conference on Materials Engineering and Environmental Science (MEES2015), World Scientific, 2016.

[45] E. Papirer, Adsorption on Silica Surfaces, CRC Press, Florida, United States, 2000.

[46] J. Motuzas, A. Julbe, R.D. Noble, A. van der Lee, Z.J. Beresnevicius, Rapid synthesis of oriented silicalite-1 membranes by microwave-assisted hydrothermal treatment, Microporous Mesoporous Mater. 92 (2006) 259–269.

[47] M. Ghamami, L.B. Sand, Synthesis and crystal-growth of zeolite (NH₄, TPA)-ZSM-5, Zeolites 3 (1983) 155–162.

[48] R. Karimi, B. Bayati, N.C. Aghdam, M. Ejtemaee, A.A. Babaluo, Studies of the effect of synthesis parameters on ZSM-5 nanocrystalline material during template-hydrothermal synthesis in the presence of chelating agent, Powder Technol. 229 (2012) 229–236.

[49] Min Liu, Junhui Li, Wenzhi Jia, Mengjiao Qin, Yanan Wang, Kai Tong, H. Chen, Z. Zhu, Seed-induced synthesis of hierarchical ZSM-5 nanosheets in the presence of hexadecyl trimethyl ammonium bromide, RSC Adv. 5 (2015) 9237–9240.

[50] G. Majano, A. Darwiche, S. Mintova, V. Valtchev, Seed-induced crystallization of nanosized Na-ZSM-5 crystals, Ind. Eng. Chem. Res. 48 (2009) 7084–7091.

[51] Y. Yan, M.E. Davis, G.R. Gavalas, Preparation of zeolite ZSM-5 membranes by in-situ crystallization on porous α-Al₂O₃, Ind. Eng. Chem. Res. 34 (1995) 1652–1661.

[52] J.M. Kremsner, C.O. Kappe, Silicon carbide passive heating elements in microwave-assisted organic synthesis, J. Org. Chem. 71 (2006) 4651–4658.

[53] S. Sen, R.R. Wusirika, R.E. Youngman, High temperature thermal expansion behavior of H[Al]ZSM-5 zeolites: the role of Brønsted sites, Microporous Mesoporous Mater. 87 (2006) 217–223.

[54] C.O. Kappe, Unraveling the mysteries of microwave chemistry using silicon carbide reactor technology, Acc. Chem. Res. 46 (2013) 1579–1587.

[55] H. Li, A. Elmoataz, J.M. Fadili, S. Ruan, An improved image segmentation approach based on level set and mathematical morphology, Proceedings of the Third International Symposium on Multispectral Image Processing and Pattern Recognition (2003) 851–854.