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Bioinspired Rattan-Derived SiSiC/Zeolite Monoliths: Preparation and Characterisation

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Dedicated to the late Denise Barthomeuf, George Kokotailo and Sergey P. Zhdanov in appreciation of their outstanding contributions to zeolite science

Abstract

In the present article, a three-step process for the preparation of SiSiC/zeolite composites is presented. Rattan-derived SiSiC composites were obtained via a two-step biotemplating liquid silicon infiltration process (LSI). The LSI process, consisting of pyrolysis of the biotemplates (Rattan stems) followed by reactive infiltration of the carbon preforms with liquid silicon at 1550 °C, led to the formation of SiSiC ceramic composites. The SiSiC replicas (59 wt.% of SiC, 40 wt.% of solidified Si, 1 wt.% carbon) faithfully reproduced the macrostructure of Rattan and exhibited an open porosity between 20 and 40 vol.%, with unidirectional parallel microchannels in the range of ~100–300 μm in diameter. In a third stage **MFI**-type zeolite (Silicalite-1 and ZSM-5) coatings were developed on the SiSiC ceramic supports via a partial conversion of the substrate into zeolite (support self-transformation method). The metallic Si in the support was partially dissolved under hydrothermal conditions in a reaction mixture consisting of deionised water, template (TPABr) and NaOH, but without any external Si-source. The influence of different synthesis parameters in the development of the zeolite coating is discussed in detail. The resulting products were characterised by X-ray diffraction, TGA, N_2 adsorption/desorption and SEM-EDX. The filtrates were analysed by ICP-OES. SEM and adsorption measurements revealed that biomorphic cellular SiSiC/zeolite composites possess bimodal (micro-/macro-) porosity. In the final SiSiC/zeolite composite, a maximum zeolite loading up to 40 wt.% was calculated on the basis of TGA and XRD analyses. Thermal shock tests showed that a good coating adherence to the SiSiC substrate was obtained. In addition, a SiSiC/ZSM-5 monolith was also tested as structured catalyst for *n*-hexane cracking.

Keywords: Bioinspired SiSiC/zeolite composites; Biomorphic ceramics; **MFI** zeolite; Monolithic reactors; Microreactors

1. Introduction

Anisotropic cellular ceramic materials with hierarchical porosity ranging from the nanometre to the millimetre scale are interesting for applications as filters, catalysts or catalyst supports, membranes, and adsorbents [1]. The cellular architecture of native lignocellulosic materials, such as biological fibres and wood tissue, is characterised by hierarchically built anatomies, complex architectures and uniaxial anisotropic open porosity with a broad variety of cellular/porous patterns, unique structural–mechanical properties, and functional designs, resulting from a long genetic evolution process [1–4]. Therefore, as an alternative to conventional extrusion technologies, biotemplating or bioinspired methods have been developed in order to finely replicate the hierarchical porous structures of such biological materials for the development of ceramic materials [1]. Inorganic replicas (SiOC [2], SiSiC and SiC [1–8], SiO_2 [9], zeolite [10], TiO_2 [11], ZrO_2 [12], Al_2O_3 [13], YZS [14], TiC

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and ZrC [7]) were fabricated starting from different natural/biological materials.

SiC-based ceramics and composite materials exhibit attractive properties, such as excellent mechanical strength at high-temperature, high thermal conductivity and good oxidation and corrosion resistance. Therefore, SiC and SiSiC materials are nowadays of high interest for various frictional and structural applications (as dense structures) [15], or high-temperature filters or catalyst supports (as porous structures) [16,17]. Biomorphic microcellular SiSiC ceramics can be manufactured by vapour silicon infiltration [18] or liquid silicon infiltration (LSI) of the pyrolysed structure of lignocellulosic [1]. The LSI of biocarbon templates derived from plants (biocarbon (C_B) templates) is able to reproduce the micromorphology of the native tissue with high precision in the SiSiC ceramic composite, representing a net-shape process on the micrometer scale. Due to their hierarchical anisotropic morphology with unidirected pore structures on the micrometer level and outstanding properties, cellular biomorphic SiSiC ceramics obtained via LSI have a great potential as supports for catalysts [3,4]. The functionalisation of SiSiC ceramics with zeolite yields composites with multimodal micro-/macroporosity [17].

Zeolites are crystalline aluminosilicate molecular sieves. Due to their ordered microporous network (diameter below 1.3 nm), large specific surface area, ion-exchange properties and acidity, zeolites are extensively used in industrial ion-exchange, adsorption, separation and catalytic applications [19]. Zeolite-coated structured composites [20] were utilised as sensors [21], vehicle emission control systems [22], units for the treatment of exhaust gases [23], structured catalytic packings or monoliths for novel reactor concepts [24–26], adsorption/separation units (e.g. membranes) [27,28]. Up to now, different porous substrates (made of ceramic, metal and glass) were utilised in the form of foams, honeycombs, packings, beads, etc. [20]. Generally, the fabrication of zeolite coatings was performed by in-situ hydrothermal synthesis [25], seeding techniques [28], dip-coating [23], or adsorption of zeolite crystals onto chemically functionalised supports [21].

One particular type of conventional hydrothermal synthesis of zeolite coatings is the in-situ crystallisation in the presence of active or reactive supports (support self-transformation) [17,29–39]. Part or all of the framework builders for the zeolite crystallisation are initially present in the carrier and not in the precursor solution [17]. The nutrients (Si and/or Al) for the zeolite synthesis are dissolved from the substrate into the solution phase during the hydrothermal treatment and utilised for the crystallisation process. This method was recently used to partially transform glass discs and beads into zeolite (**MFI** and **BEA**) containing composites, in order to develop membranes for separation and composite beads for catalysis. The substrate provides SiO_2, Al_2O_3 and, in some cases, B_2O_3, for the zeolite crystallisation. Most importantly, the entire support could be transformed into a structured zeolite body, which preserves the shape and architecture of the original support [29–34]. Rauscher et al. [30] postulated that the hydrothermal transformation of porous glass granules into ZSM-5 granules occurs in three stages: partial dissolution of porous glass granules up to the saturation of silicon in the solution phase, adsorption or complexation of Al onto the surface of porous glass granules and total transformation of amorphous porous glass granules into crystalline ZSM-5 granules. Aluminium foams were also used as active supports for the development of ZSM-5 coated monolithic reactors [35]. Sintered honeycomb bodies of mullite and silica glass were subjected to hydrothermal treatments in presence of template and sodium hydroxide, yielding mullite/zeolite composites [36–38]. Similarly, we also prepared **MFI**-type zeolite coatings on polymer-derived ceramic foams, with the substrate supplying only the SiO_2 for the crystallisation [39].

Very recently, we published our preliminary results on the preparation of bioinspired Rattan-derived SiSiC/zeolite ceramic composites via a combination of LSI for the fabrication of the SiSiC ceramic supports and self-support transformation for the development of the zeolite coating [17]. The objective of the present paper is to provide insight into the preparation and characterisation of the Rattan-derived SiSiC/zeolite composites. The influence of different parameters (template concentration, synthesis time, Si/Al ratio, and crystallisation temperature) is discussed. The applicability of the Rattan-derived SiSiC/zeolite composites as structured monolithic catalysts for heterogeneous catalytic reactions is also shown.

2. Experimental

2.1. Rattan-derived SiSiC support preparation

Specimens of dried native Rattan were cut, shaped into cylinders of the desired size (length 5.7 cm and diameter 3.6 cm) and polished (Fig. 1). Then, the cylindrical Rattan samples were pyrolysed in argon atmosphere at 800 °C for

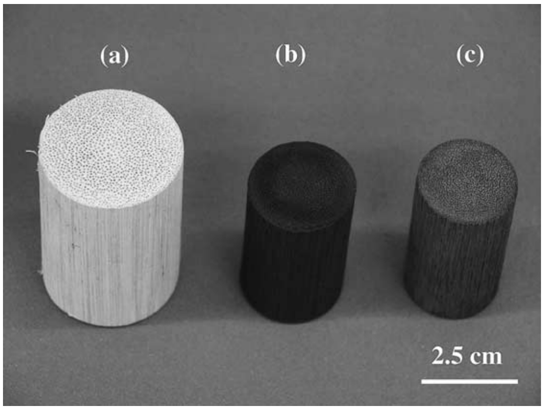

Fig. 1. Digital picture of a (a) native Rattan stem cylinder, (b) the pyrolysed biocarbon preform (C_B template) and (c) the SiSiC ceramic monolith after LSI.