



Silane functionalized open-celled ceramic foams as support structure in metal organic framework composite materials



Ulf Betke^a, Steven Proemmel^a, Stefan Rannabauer^b, Alexandra Lieb^{a,*},
Michael Scheffler^b, Franziska Scheffler^a

^a Otto-von-Guericke-University Magdeburg, Chemical Institute – Industrial Chemistry, Universitätsplatz 2, 39106, Magdeburg, Germany

^b Otto-von-Guericke-University Magdeburg, Institute for Materials and Joining Technology – Nonmetallic Materials, Große Steinertischstraße 6, 39104, Magdeburg, Germany

ARTICLE INFO

Article history:

Received 2 August 2016

Received in revised form

8 September 2016

Accepted 10 October 2016

Available online 11 October 2016

Keywords:

Metal organic framework

Ceramic foam

Composite material

Adsorption driven heat pump

Silanization

ABSTRACT

The metal organic framework (MOF) materials HKUST-1, CAU-10, MIL-101(Cr) and UiO-66(Zr) were successfully coated onto open cellular silanized alumina and oxide bonded silicon carbide foams by a direct crystallization approach. Two different silanization routes were tested with respect to the functional group of the silane molecule used. For the HKUST-1 and CAU-10 based composite materials the influence of the foam material, its pore size and pore density and its surface chemistry on the amount of deposited MOF material and its water uptake capacity was evaluated. Based on these data in combination with micro computertomography results a model was developed to estimate the MOF coating thickness on cellular supports.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Macroporous ceramic foams play an important role for current and future technologies. They are used for filtration of metal melts in foundries or as catalyst supports [1]. Several sophisticated methods for the fabrication of ceramic foams have been developed, like direct foaming approaches based on particle stabilized emulsions [2–4], or preceramic polymer melts [5–7]. However, ceramic foams are most often produced by the polymer sponge replication method established by Schwartzwalder and Somers in 1963 [8], which was also used for manufacturing the foams used within this study. One major area of research in the field of cellular ceramics is the implementation of further functionality, e. g. by application of active coatings like microporous adsorbents (zeolites, metal-organic frameworks: MOFs), onto the foam struts. As micropores we address pores according to the IUPAC nomenclature having a diameter of <2 nm [9,10], whereas the ceramic foam cells are referred to as macropores.

For zeolites and microporous silicoalumophosphates those microporous-macroporous composite type materials are well known [11–15]. However, for composites of MOFs and cellular ceramics only two examples have been described. These are Al₂O₃/SiO₂ foams coated with HKUST-1 [16] and HKUST-1 coated on ob-SiC foams activated by alkaline etching [17].

Possible utilization of these MOF@ceramic foam composites is for heat storage or in heat pumps for sorptive cooling applications using water ad- and desorption processes into the microporous compound [18,19]. In the latter case the MOF component provides a large water uptake capacity corresponding to a high heat of evaporation (for example CAU-10: 290 kW h m⁻³, MIL-101(Cr): 550 kW h m⁻³, both with H₂O as working fluid); this results in potentially high energy densities and/or chilling powers [20]. However, the transportation of mass (adsorbate) and heat is difficult to provide for MOFs in the powdery state due to their low thermal conductivity, low particle size and low density. Therefore, the coating of MOF materials on appropriate supports is mandatory for those applications.

Ceramic foams represent a convenient support material. Their irregular geometry of the macropores allows an efficient transportation of mass, i. e. the adsorptive, to the layer of microporous adsorbent due to the high degree of turbulent flow and radial

* Corresponding author.

E-mail address: alexandra.lieb@ovgu.de (A. Lieb).

mixing [21,22]. Furthermore, sorptive heat can be conducted by the foam struts avoiding hot-spots with local re-adsorption limitations during energy discharging. This actually improves the ad-/desorption kinetics and therefore results in faster cycling times and increased chilling power, when used in heat pumps.

In this work we describe a method to prepare micro-macroporous composite materials by growing a layer of the MOFs $\text{Cu}_3[\text{C}_6\text{H}_3(\text{COO})_3]_2 \cdot x\text{H}_2\text{O}$ (synonym: HKUST-1) [23], $\text{Al}(\text{OH})[\text{C}_6\text{H}_4(\text{COO})_2] \cdot x\text{H}_2\text{O}$ (synonym: CAU-10) [24], $\text{Cr}_3\text{O}(\text{OH})[\text{C}_6\text{H}_4(\text{COO})_2]_3 \cdot x\text{H}_2\text{O}$ (synonym: MIL-101(Cr)) [25] and $\text{Zr}_6\text{O}_4(\text{OH})_4[\text{C}_6\text{H}_4(\text{COO})_2]_6 \cdot x\text{H}_2\text{O}$ (synonym: UiO-66(Zr)) [26] on macroporous oxide-bonded silicon carbide (ob-SiC) and alumina (Al_2O_3) ceramic foams (CF). The cellular ceramics were surface-functionalized by a silanization procedure prior to the MOFs direct crystallization. For this purpose, silanization reactions involving trialkoxy silanes ($\text{R}^1\text{O})_3\text{Si}-\text{R}^2$ (R^1 usually CH_3 or C_2H_5) bearing a functional group R^2 , for example an aminopropyl chain, were used. These are common in the fabrication of MOF@porous ceramics based membranes [27–29]. To study the influence of the silane functional group R^2 on the direct crystallization of MOFs onto cellular ceramic substrates two procedures were carried out: The first route involved a silanization with aminopropyl triethoxysilane (APTES) followed by a reaction of the terminal $-\text{NH}_2$ moieties with terephthaloyl dichloride (Fig. 1, upper section). This results in surfaces functionalized with $-\text{C}_6\text{H}_4-\text{COOH}$ groups being chemically similar to the carboxylic acid linker molecules contained in almost all stable microporous MOFs. The second route was the direct silanization of the ceramic substrates with octyl triethoxysilane generating a surface grafted with nonpolar alkyl chains (Fig. 1, lower section).

2. Experimental section

2.1. Ceramic foam support preparation

The alumina cellular ceramic foams were prepared following the replica approach by Schwartzwalder [8]. PU templates were coated with a ceramic slurry, the template was thermally removed and the alumina particles were sintered to form the cellular structure.

The alumina slurry used to coat the PU templates was prepared as follows (all wt% values with respect to the final slurry including all components; a typical formulation starting from 100 g Al_2O_3 powder can be found in Table 1): First, an ethanolanmonium citrate based deflocculating agent (0.8 wt%, Dolapix CE 64, Zschimmer

Table 1

Standard slurry composition for the preparation of alumina cellular ceramics by the sponge replication technique (Schwartzwalder-process).

Component	wt% of slurry	Net weight/g
alumina (Almatis CT 3000 SG)	78.3	100.0
demineralized water	19.6	25.0
deflocculating agent (Dolapix CE 64)	0.8	1.0
binder (Optapix PA 4G)	1.2	1.5
antifoaming agent (Contraspum K 1012)	0.1	0.1

& Schwarz Chemie GmbH, Lahnstein, Germany) was dissolved in demineralized water (19.6 wt%), then the alumina powder (78.3 wt%, CT 3000 SG, Almatis AG, Ludwigshafen, Germany) was added. Mixing and deagglomeration were carried out in a planetary centrifugal mixer (THINKY Mixer ARE-250, THINKY Corp. Tokyo, Japan) at 2000 rpm for 15 min. Subsequently, a polyvinylalcohol based binder (1.2 wt%, Optapix PA 4G, Zschimmer & Schwarz Chemie GmbH) and a nonionic alkyl polyalkylene glycoether based anti-foaming agent (0.1 wt%, Contraspum K1012, Zschimmer & Schwarz Chemie GmbH) were added. The slurry was mixed for 15 min at 2000 rpm a second time and cooled to room temperature before further processing. As polymer sponge templates polyester polyurethane foams with a cell count of 20 ppi (pores per inch) and 30 ppi and a geometrical size of 15 mm × 15 mm × 20 mm (Koepf Schaum GmbH, Oestrich-Winkel, Germany) were used. The PU sponge pieces were immersed into the ceramic suspension to fill up the pores of the template completely. Afterwards the excess amount of slurry was removed manually by squeezing the foam template until its weight reached approximately 2.0 g (corresponding to ~89% porosity in the final foam piece). Remaining closed pores were opened by carefully blowing air through the slurry-coated PU foam. The coated foams were dried under ambient conditions for 24 h. Removal of the PU template was performed thermally in three steps (110 °C/2 h, 250 °C/3 h, 400 °C/3 h) in a circulating air furnace (KU 40/04/A, THERMCONCEPT Dr. Fischer GmbH, Bremen, Germany). To avoid cracks in the ceramic material caused by gaseous decomposition products of the PU template low heating and cooling rates of 1 K/min were applied. After burning away the polymer foam the samples were transferred into a sintering furnace (HTL 10/17, THERMCONCEPT Dr. Fischer GmbH, Bremen, Germany). Last remains of PU template and binder were oxidized at 600 °C for 3 h. Afterwards the ceramic foams were densified by sintering for 3 h at 1650 °C in air. In order to avoid thermally induced cracking, heating and cooling rates were maintained at 3 K/min. Due to the shrinkage during sintering the

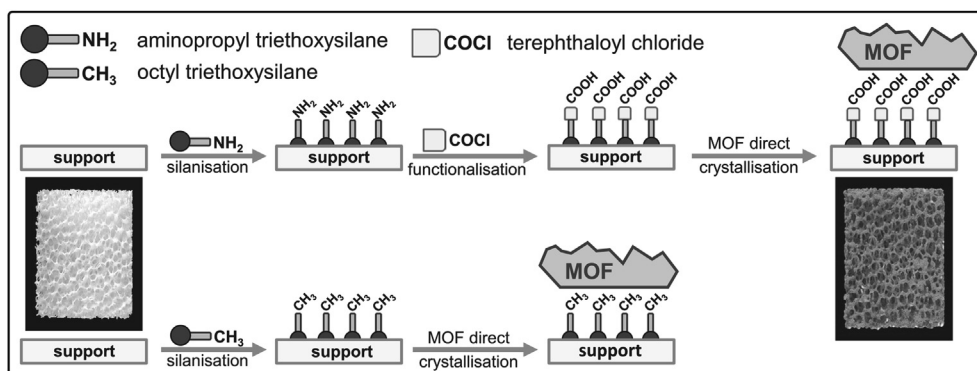


Fig. 1. Processing scheme of the silanization based functionalization of cellular ceramics. *Top row:* “Polar functionalization”: After coating with a silane bearing a reactive $-\text{NH}_2$ group the reaction with terephthaloyl dichloride is carried out under formation of a peptide bond. After hydrolysis of the remaining $-\text{COCl}$ moiety a substrate grafted with polar carboxyl groups is generated. *Bottom row:* “Nonpolar functionalization”: Treatment of the ceramic foams with octyl triethoxysilane results in a surface modified with nonpolar alkyl chains. Both routes are applied to ob-SiC and alumina ceramic foams.

Download English Version:

<https://daneshyari.com/en/article/4758528>

Download Persian Version:

<https://daneshyari.com/article/4758528>

[Daneshyari.com](https://daneshyari.com)