ELISABETE RIBEIRO SILVA[1)*)], NUNO CORREIA[1)], JOAO MIGUEL SILVA[2)], FERNANDO A. COSTA OLIVEIRA[3)], FERNANDO RAMOA RIBEIRO[1)], JOAO CARLOS BORDADO[1)], MARIA FILIPA RIBEIRO[1)]

Manufacture of cordierite foams by direct foaming

Summary — Open cell cordierite foams were prepared by a direct foaming two-component polyurethane (PUR)/ceramic system. Through optimization of several experimental parameters, such as contents of catalyst, and ceramic cordierite precursor, as well plasticizer presence, foams with porosities 85—95 % and densities ranging from 130—410 kg/m^3 were obtained. These foams characteristics make them attractive to be used as catalyst supports. The new two-component PUR/ceramic system developed allows the high solid's loading (higher than 40 wt. %). Finer ceramic particles in this system provide better particles' package and cohesion upon sintering, favouring the cordierite foam stability.

Key words: cordierite foams, polyurethane, direct foaming, porosity, density, cellular structure.

OTRZYMYWANIE PIANEK KORDIERYTOWYCH METODĄ BEZPOŚREDNIEGO SPIENIANIA

Streszczenie — Pianki kordierytowe o otwartych komórkach otrzymywano na drodze bezpośredniego spieniania dwuskładnikowego układu poliuretan (PUR)/materiał ceramiczny stanowiący prekursor kordierytu (rys. 1). Metodami analizy termograwimetrycznej (TGA) oraz różnicowej analizy termicznej (DTA) scharakteryzowano przebieg termicznej degradacji układu PUR/prekursor kordierytu w atmosferze utleniającej (rys. 2). Na drodze optymalizacji niektórych parametrów doświadczalnych, mianowicie zawartości katalizatora (dibutylolaurynianu cyny — DBTL) i prekursora kordierytu a także obecności lub braku plastyfikatora (ftalanu dioktylowego — DOP) uzyskiwano pianki o porowatości 85—95 % i gęstości zawartej w przedziale 130—410 kg/m^3 (tabela 2). Pianki o takich właściwościach dobrze nadają się do zastosowania w charakterze nośników katalizatorów. Opracowany nowy dwuskładnikowy układ PUR/prekursor kordierytu pozwala na wytwarzanie pianek o dużej zawartości (do ok. 50 % mas.) materiału ceramicznego. Metodą rentgenograficzną oraz za pomocą skaningowej mikroskopii elektronowej scharakteryzowano strukturę i morfologię uzyskanej pianki (rys. 3 i 4). Stwierdzono, ze im mniejsze są wymiary cząstek ceramicznego prekursora kordierytu (ok. 5 mm) w mieszaninie z PUR, tym korzystniejsze staje się upakowanie i kohezja cząstek ceramicznych po spiekaniu, dzięki czemu polepszeniu ulega stabilność końcowej pianki kordierytowej.

Słowa kluczowe: pianki kordierytowe, poliuretan, bezpośrednie spienianie, porowatość, gęstość, struktura komórkowa.

CERAMIC FOAMS — GENERAL CHARACTERISTICS

Over the past few years there has been observed an increasing interest in developing of new processing routes for the production of ceramic foams and in the improvement of the existing ones. This is associated mainly with the inherent properties that these materials can offer, such as high permeability, high specific strength, low density, low thermal conductivity, high thermal shock resistance, high porosity, high resistance to chemical corrosion and high tortuosity factor [1].

Ceramic foams are often divided into two categories, namely the open-cell and the closed-cell foams, which make them suitable for different applications.

The present work focuses on the development of open-cell foams, which are highly versatile porous materials used mainly in applications which require fluid transport in the microstructure. Among these applications there are the ones in the field of solid-fluid separation (metal melt filter, exhausted gas filter), porous burner, gas diffuser, flame barrier, bone replacement, aeration of liquids, refractories, lightweight structures, and catalyst supports [1]. The last application is the ultimate goal of our work, which is to fabricate the supports for depositing metal zeolites suitable for catalytic combustion of volatile organic compounds (VOCs). Indeed, this type of material favours the flow turbulence within the structure thereby secures good reactant's mixing and radial dispersion.

Several reviews on ceramic foams processing and their characterization have been recently published

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[1)] Instituto Superior Técnico, Departamento de Engenharia Química, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.
[2)] Instituto Superior Engenharia de Lisboa, Departamento de Engenharia Química. Av. Cons. Emídio Navarro, 1950-062 Lisboa, Portugal.
[3)] Instituto Nacional de Engenharia, Tecnologia e Inovção, Departamento de Materiais e Tecnologias de Produção, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal.
[*)] e-mail: elisabetesilva@ist.utl.pt

[1—6]. Many techniques exist to produce the cellular ceramics. They can be made among others by gel casting, *in situ* polymerization, addition of porophors, rapid prototyping, foaming of aqueous slurries and infiltration of open-cell polymer foams. The latter technique also known as the polymer foam replication process, first patented by Schwartzwalder and Somers in 1963 [7], was recently applied to the fabrication of cordierite foams [8]. Briefly, cordierite-based open-cell foams were fabricated by immersion of polymeric foams, usually open-cell polyurethane templates, followed by removal of slurry excess. The polymer is then burned out and the ceramic body is sintered to yield a replica of the original foam.

One of the drawbacks of this process is that the resulting foams consist of hollow struts with sharp edges, due to the burnout of the polymeric template [9]. The presence of such defects is critical for the mechanical properties.

Alternative processing routes rely on foaming of ceramic slurries by mechanical agitation or *in situ* evolution of gases [10—13]. These processes are also referred as direct polymerization or direct foaming. The foams produced by these methods are characterized by dense struts in the foam structure [1]. These morphological features influence the mechanical properties of the ceramic foams [3].

This paper describes a method similar to existing ones [14, 15], based on foaming of a two-component polyol-isocyanate mixture, in which ceramic particles are dispersed. A wide range of ceramic foams could be obtained in this process, depending on a number of parameters, such as relative density, cell morphology, characteristics of the struts between the pores, as well as pore morphology (isotropic or anisotropic pores), size and distribution. Since the properties of foams are related to the nature of the ceramic material itself, it becomes important to improve the methods, so that new and attractive materials can be developed.

Cordierite material has been selected, due to its low cost, availability and its special properties, in particular its low thermal expansion coefficient ($2.6 \cdot 10^{-6}$ K^{-1}), good resistance to thermal shock ($R > 250$ K) and reasonable strength (60—90 MPa), which make it attractive for high temperature catalyst supports [16]. Scarce information concerning direct foaming methods for fabricating cordierite foams has been reported. This kind of system is difficult to stabilize, in view of the complex mix of ceramic cordierite precursors.

In this paper we propose a new method to produce cordierite foams by direct foaming.

EXPERIMENTAL

Materials

Two-component polyurethane (PUR) foam systems were developed.

The first component, so called resin, consisted of formulated mixture of polyols, catalysts, surfactants and blowing agents. A range of "Alcupol" polyether polyols produced by Repsol YPF, with molecular weight between 400 and 4800 g · mol^{-1}, hydroxyl number in the range of 100—300 mg KOH/g and hydroxyl functionality between 2 and 4, were used, such as "Alcupol D-1011". As catalysts DBTL (dibutyltin dilaurate) from Merck was used. As cell stabilizers usually a polyoxyethylene/methylpolysiloxane copolymer "Tegostab B-8423" produced by Tegostab was applied. Water was added to produce (from diisocyanate) CO_2 as blowing agent.

In addition, to lower the viscosity of the two-component system, to the polyol component a plasticizer from Sigma-Aldrich — DOP (dioctyl phthalate) was added.

The second component was a grade of polymeric diphenyl methane diisocyanate (crude MDI-E) from DOW Portugal, Lda., with NCO content of 31.4 %.

The two-component polyurethane foam systems are available on market, but we anticipated that they could not withstand high solid loads.

The ceramic powder selected for this study as a precursor of cordierite was a powder mixture of materials (ball clays, talc, alumina and silica provided by Rauscher Portuguesa Lda.). This powder form upon firing cordierite characterized with a specific surface area of 11 $m^2 \cdot g^{-1}$ (measured by "Monosorb MS10", Quantachrome Corporation, USA), an average particle size of 4.5 μm (measured by apparatus "CILAS 1064", France) and a real density of 2.91 g · cm^{-3} (measured by "AccuPyc 1330" Helium pycnometer, Micrometrics Int. Corp., USA).

Foam preparation

The sequence steps of the method are depicted in Fig. 1. The first step is the formulation of the two components of the systems, which consist essentially of the mixture of the ceramic particles within each component — isocyanate and polyol.

The cordierite precursor powder was ground to guarantee that the agglomerates were below 125 μm. Afterwards, addition of the ceramic to the polymeric reagents was accomplished by mixing at high stirring rate (more than 900 rpm) in order to disperse the particles.

In addition, some of the foams were prepared by milling the mixture of ceramic particles and polyol in a ball mill for 24 h what gave particle size lower than 5 μm.

After obtaining a homogeneous mixture of the foam components with the ceramic particles, the other additives were added to the polyol component to constitute the resin. Then both components were combined and stirred at a rate higher than 900 rpm, for less than 1 minute. The mixture was then poured into a polyethylene board mold (15×15×15 cm), allowing the foam to rise freely. The foam was left at room temperature in the

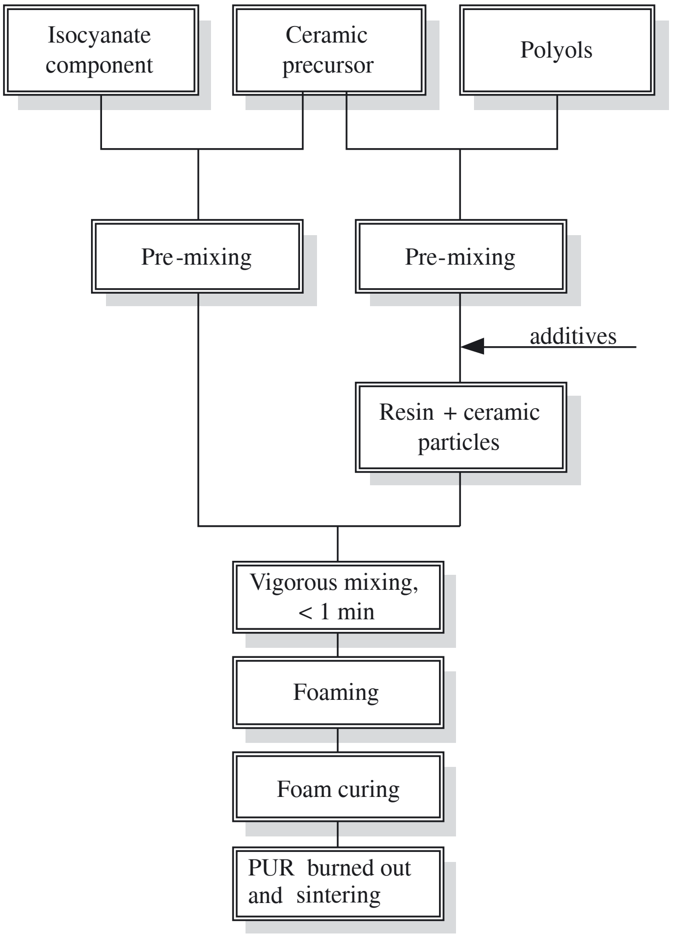

Fig. 1. Sequence of the steps of the direct foaming method to produce ceramic foams

mold, for at least 24 h, to ensure the reaction (cure) is completed.

Different contents of ceramic particles were applied, ranging from 5 to 60 wt. %, in the two-component systems. Consequently, it was necessary to optimise some experimental parameters, namely the content of blowing agent precursor, contents and types of catalysts and surfactants in order to prevent the cracks and foam collapse. A formulation example (sample D from Table 2) is depicted in Table 1.

Table 1. Formulation of D sample

	Polyol component (resin)	Content, wt. %1)
1	"Alcupol D-1011" — polyol	100
	"Tegostab B-8423" — surfactant	1
	DBTL-catalyst	0.4
	Water	4
2	Isocyanate component	
	Crude MDI-E	108
3	Ceramic powder2)	42

1) Contents based on 100 % of polyol.
2) Content of ceramic powder in the total formulation, which was mixed in half with each component.

The polymer-ceramic foams obtained were cut into cubes, and the polymer substrate was burned out at static air, in a temperature programmable furnace, at a heating rate of 1 °C min^{-1} to 500 °C with a dwell time of 1 h, followed by heating at the same rate until 1000 °C with a dwell time of 1 h.

Sintering of the resulted ceramic body was carried out in a gas furnace at 1300 °C, providing the densification of the ceramic network.

Foams characterization

In order to evaluate the burnout schedule of the polymer substrate thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on PUR/ceramic foams. A "Setaram TG-DSC92" thermobalance was used with a flow rate of air of 30 ml · min^{-1} and a heating rate of 1 °C · min^{-1}.

The bulk density of foam was determined from the weight-to-volume ratio.

The true density of the sintered ceramic foam was measured in a He pycnometer, "Accupyc 1330", Micrometrics Inst. Corp., USA.

The microstructure of the cordierite ceramic foam was characterized by X-ray diffraction (XRD) using a Bruker, D8 Advance Bruker diffractometer (Cu Kα, wavelength = 1.5406 Å, 40 kV, 30 mA).

The PUR/ceramic foam morphology was evaluated by optical analysis, using a Wild Heerbrugg optical microscope and the sintered foam morphology was assessed by scanning electron microscopy (SEM), using a Hitachi S-2400 scanning electron microscope, with a 15 kV beam.

RESULTS AND DISCUSSION

The thermal degradation of a representative polyurethane-ceramic (PUR/ceramic) foam in an oxidative environment is showed in Fig. 2. In a first stage which is characterized by the highest weight loss rate its weight loss starts at a temperature range of about 180 °C until 300 °C; the total weight loss at this stage equals 31 wt. % (see curve 1). A second stage is observed between 300—400 °C, and is characterized by a slow weight loss of about 9 wt. %. Further thermal degradation proceeds until 500 °C, with a weight loss of 18 wt. %. Above this temperature the weight remained unchanged. The total decomposition reached about 58 wt. %, which is associated to the degradation of the PUR organic phase in the foam, since the thermal analysis of ceramic precursor (results not showed) did not present any significant thermal decomposition.

The reactions involved in the PUR decomposition appear as two main exothermic peaks in the temperatures ranges of about 200—300 °C and 380—500 °C (see curve 2), which are associated with the highest weight loss rates. We can conclude that thermal treatment under an

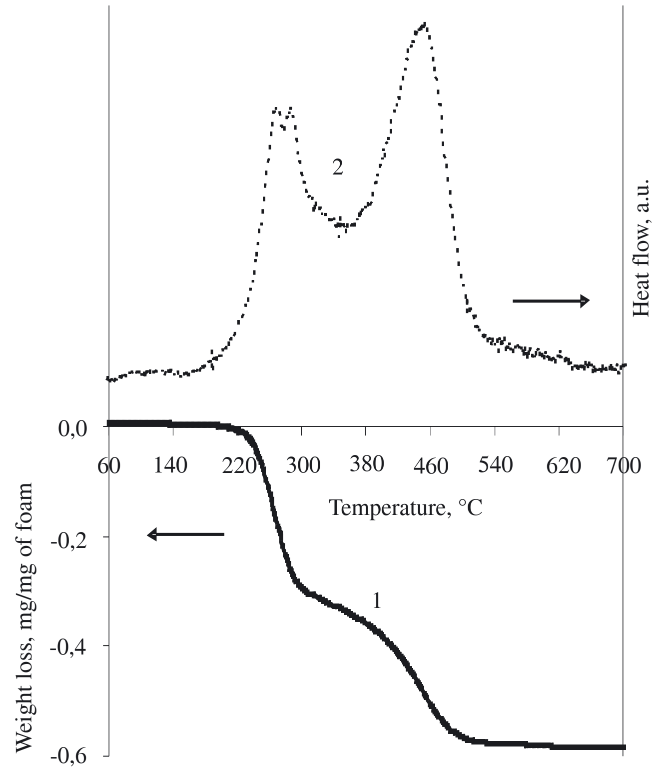

Fig. 2. Thermogravimetric (1) and differential thermal data (2) of PUR/ceramic foam E under an air flow

T a b l e 2. Processing details and properties of foams

Sample[1]	Polyol		Catalyst	Plasticizer	Ceramic precursor	PUR/ceramic foam	Cordierite foam	
	"Alcupol D-1011"		DBTL[3] wt. %	DOP[3] wt. %	solid[4] wt. %	ρ_{ap} kg·m^{-3}	ρ_{ap} kg·m^{-3}	ε[8] %
	g·mol^{-1}	mg KOH · g^{-1}						
A[5]	<400	280	0.5	—	45	79	407	84.5
B	>1000	110	0.4	>10	48	168	251	94.0
C	>1000	110	0.5	—	30	52	177	93.5
D	>1000	110	0.4	—	42	103	224	91.4
E[6]	>1000	110	0.3	—	42	94	127	95.2
R[7]	—	—	—	—	60	—	350	85.0

[1] All the samples were prepared with Crude MDI-E (NCO content of 31 wt. %).
[2] Molecular weight and hydroxyl number of the polyol.
[3] Contents based on 100 % of polyol.
[4] Solid content in two-component system or in aqueous suspension for the replication sample.
[5] This sample was prepared with "Alcupol D-0411" polyol.
[6] Solid particles previously milled with the polyol component.
[7] Sample prepared by the replication method.
[8] Estimated porosity (ε): $\varepsilon = (1 - \rho_{ap}/2600\ \mathrm{kg \cdot m^{-3}}) \cdot 100$, where ρ_{ap} = apparent density.

oxidative atmosphere up to 500 °C is enough to PUR burnout, but we perform the treatment until 1000 °C to guarantee that the resulting ceramic foams show enough strength to be handled.

XRD patterns (results not shown) revealed that the sintered foams consisted mainly of α-indialite, according to the ICDD database. In addition, traces of mullite, alumina and quartz were also identified.

Using this direct foaming method, it was possible to prepare cellular ceramic foams, showing several reticulation degrees, different porosities, densities and pore distributions, depending on solids' loading and additives used.

Some examples of properties of representative foams obtained by this method are shown in Table 2. It is possible to observe that some foams produced by the direct foaming method show porosity and density similar to those obtained by the replication method (A *vs.* R). But that way we could not reach so well uniform and open cell structure, even if reasonable porosity was reached. Uniform foams structures with higher porosity, but lower densities, can only be obtained after some parameters optimization, as content of catalyst (in a range of about 0.3 to 1 %) and type of polyol. Work is in progress to improve the strength of the struts by increasing their density.

The content of ceramic precursor in the two-component system plays also a key role. The increase in solid loadings does not necessarily result in a decrease in porosity (see samples B *vs.* C). These two foams have similar porosity, but in B it was possible to reach a higher density, associated to the higher solid content. Nevertheless, this higher solid content in B foam was only possible with the addition of plasticizer, in order to decrease the viscosity, facilitating good components mixing. The content of plasticizer needed was higher then 10 wt. %, but the use of this additive resulted in an unsuitable structure (Fig. 3), since it has not an uniform and reticulated structure, which is required for a good catalyst support. Therefore, plasticizer content had to be decreased as it limited the amount of solid loading that

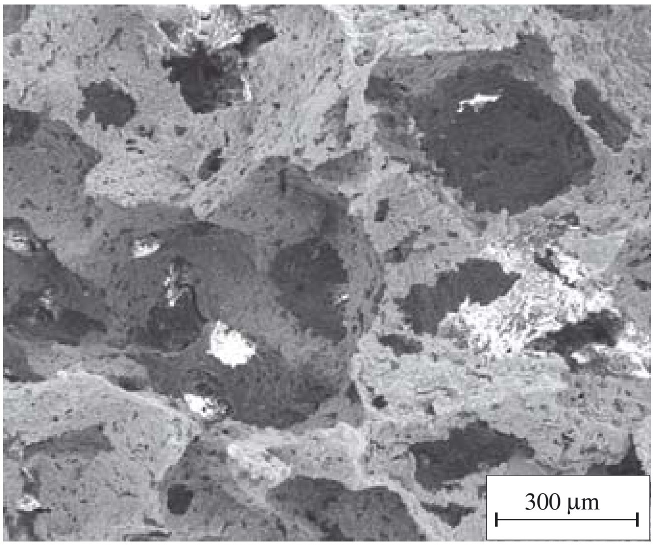

Fig. 3. SEM image of B cordierite foam

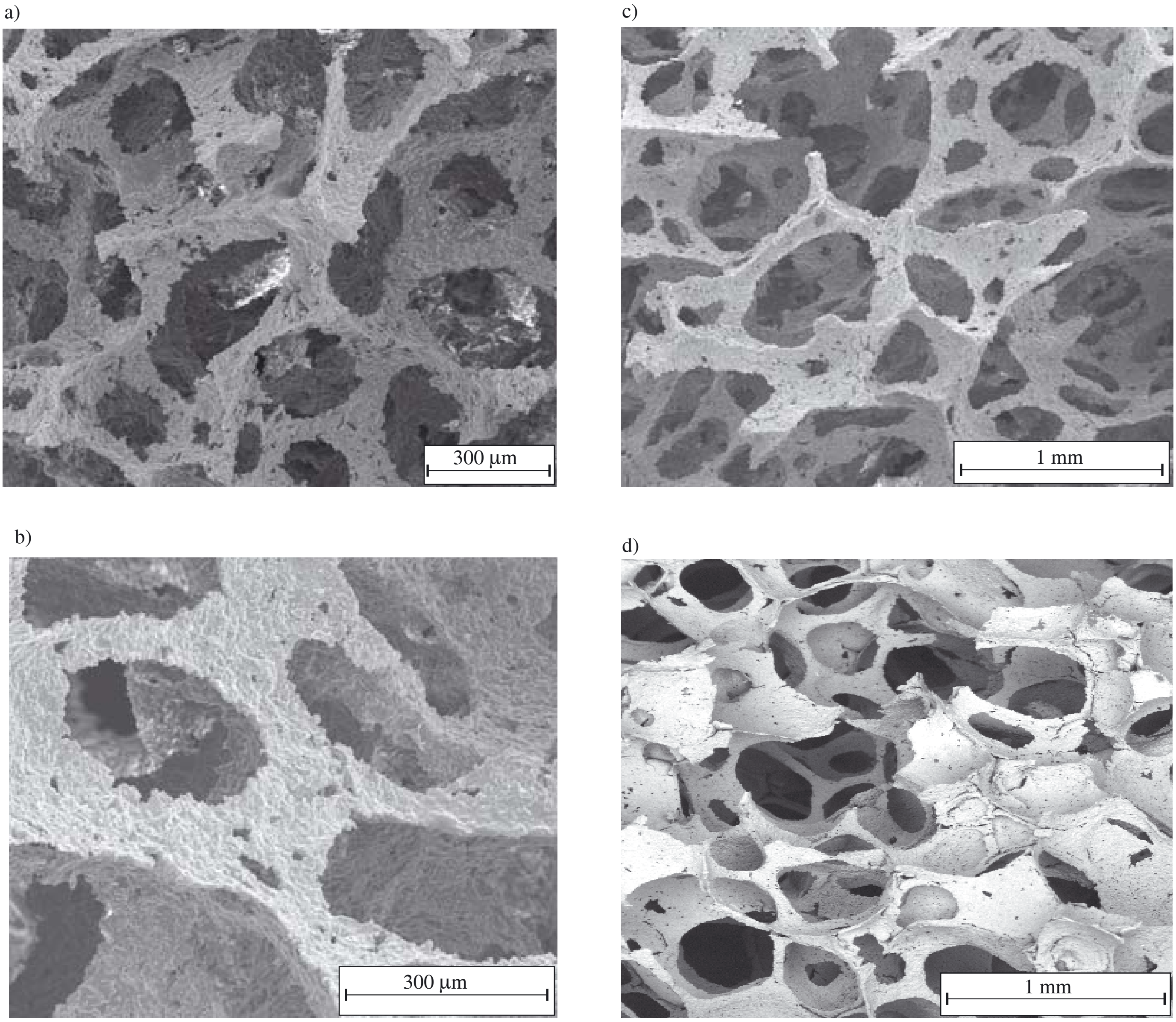

Fig. 4. SEM images of cordierite foams: a) foam D with coarser particles; b) and c) — foam E with fine particles; d) — foam R obtained by replication method

could be reached. For solid loads lower than 30 wt. %, the resulting ceramic foams were very fragile and most of them collapsed during burnout of the PUR foam.

Another experimental parameter tested in our samples was the particle size effect. Comparing D and E foams, prepared with the same solid content (Fig. 4a, b), it can be seen that previous milling of ceramic particles in the polyol component (foam E, Table 2), providing a particle size lower than 5 µm, favours higher porosity and lower density of the ceramic foam. This result seems to show that better dispersion and cohesion between particles are reached for lower particles sizes, also favouring better viscosity, which lead to PUR/ceramic foam with lower densities, giving more porous ceramic foams.

Figure 4c shows the microstructure of fracture surfaces of sintered ceramic foams observed by scanning electron microscopy. The micrographs revealed that the ceramic foams consist of a three-dimensional array of struts, with polyhedral cell shape, mainly open cells. The density and the size of these open cells are higher than the ones obtained by the replication method (Fig. 4d).

SEM observations also revealed that no hollow struts can be found, even though the cells' walls present some porosity, due to its walls unfilled by ceramic particles. The poor densification of the struts is related to the elimination of the polymer: when burning, the polymer leaves voids that cannot be filled by the ceramic during sintering. Fig. 4a shows that coarser agglomerates lead to foams with larger voids present in the ceramic walls. The finest particles are evidently more mobile than the coarser ones, leading to better particle package and cohesion in the sintering step, favouring the increase in ceramic foam stability. Even so, a ceramic foam prepared with finest particles (see Fig. 4b), contains cell walls unfilled by ceramic particles, which we associate to undispersed agglomerates, since part of the ceramic particles were also added to the isocyanate component, which could not be previously milling due to its high reactivity. Furthermore, concerning some processing details, the procedure used for mixing of the components of PUR/ceramic system does not provide the high shear stress known to be needed to break up the agglomerates in the ceramic powders [17]. Even if we used high mechanical dispersion in the two-component system, the time permitted for mixing of these two components is limited by the onset of reactions, which takes few seconds.

Another parameter which plays a critical role in the fabrication process by direct foaming is the type and content of surfactant that is needed to stabilize the PUR system. The main role of the surfactant is to guarantee the stability of bubbles until a sustainable foam structure is reached. With the increasing solid content, a high surfactant content and often stronger surfactant is needed, *i.e.*, with more capability to decrease bubbles surface tension, now surrounded by solid particles. A good compromise among all key experimental factors involved in the process is required to obtain the desired foam properties.

CONCLUSIONS

A direct foaming method was applied to a cordierite ceramic precursor, allowing to obtain cordierite ceramic foams with a reticulated structure possessing polyhedral cell shape, similar to the one obtained by the replication method, but with higher porosity, what make them attractive as catalyst supports. The effects of the content of solids, particle size and presence of plasticizer on the structure of the cellular cordierite foams were examined. More work is needed to optimize the properties of these materials, as low solid contents (<30 %) led to porous fragile struts, most of which collapsed during PUR burnout, and with higher solid contents unsuitable foams are obtained. In order to avoid the unfilled cells walls, it is important to increase the density of ceramic foams, by adding not only a plasticizer but also coupling agents (not used in this work), which could promote the inorganic filler dispersion and also the increase in solid content in the system.

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