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Influence of cryogenic drying conditions on hierarchical porous structure of aluminum oxide systems

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ABSTRACT

Highly porous alumina systems were aimed to produce by low energy-consuming sol–gel and freeze drying techniques. A 3D molecular gel structure derived by sol–gel method is provided as a precursor for vacuum freeze drying process. The typical inorganic precursor is an aqueous colloid solution such as sol or suspension. The new type of precursor results in a new columnar pore structure. The porous system keeps their high porosity even above 1500 °C in contrast with the reported heat resistance value (<800 –1000 °C) of the porous alumina systems. The effects of the solvent content and other chemical additives as well as the drying conditions were studied on the porous structure. 3D SEM images represent the inner structure of porous materials.

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1. Introduction

The aim of this study was to synthesize highly porous alumina systems by a new, efficient, low cost method avoiding the expensive supercritical extraction. Porous alumina materials are capable of providing thermal insulation over a large temperature range and possess various applications in the field of heterogeneous catalysis. The new process is based on sol–gel and freeze drying techniques. Freeze drying, also known as lyophilization, has been widely used to prepare porous materials. The gel product obtained by freeze drying process is known as a cryogel. The possibility to avoid a liquid vapor interface requires that the liquid must first be frozen and then sublimed in vacuum [1–4]. The pore size, the pore volume and the pore morphology are dependent on the variables such as freeze temperature and rate, solution concentration, nature of solvent and solute [1–4].

The typical synthesis route of cryogels is starting from aqueous suspensions, slurries [5–13]. The freezing of the aqueous suspension is followed by sublimation of the frozen phase and subsequent sintering yields ceramics granules. There are just few articles about freezing gels with 3D network [14,15]. In our preparation technique, the precursor materials of the vacuum freezing are wet gels (alco- or hydrogels) instead of liquid suspensions. The use of 3D gel structures prepared from solutions ensures the homogeneity of the products and supports to avoid the intensive crystallization and preserves the porous structures. The other novelty in the present research work is the use of non-aqueous solvents; methanol and propanol. Only a small attention has been paid to the investigation of the solvent's effect in the literature owing to the limited solubility of inorganic salts in organic solvents (e.g. in alcohols) [5,9,16,17].

The present paper introduces the novel sol–gel and freeze drying technique developed for the procedure of porous alumina. The effects of the solvent content and other chemical additives as well as the drying conditions (pressure and rate of freezing) were studied on the porous structure. The pore systems of the cryogels have been characterized by 2-3D SEM, TEM, and adsorption measurements. The bond system and the supramolecular structure of the cryogels have been determined by Al MAS NMR spectroscopy and wide angle X-ray scattering, respectively.

2. Experimental

2.1. Preparation of aluminum oxide cryogels

The aluminum-containing hydrogel was synthesized by sol–gel technique starting from an aluminum salt ($Al(NO_3)_3 \cdot 9H_2O$, at, Aldrich) and an organic solvent (1-propanol) [18]. The propanol has been used in 10–20 molar ratios of propanol/Al nitrate. Our sol–gel

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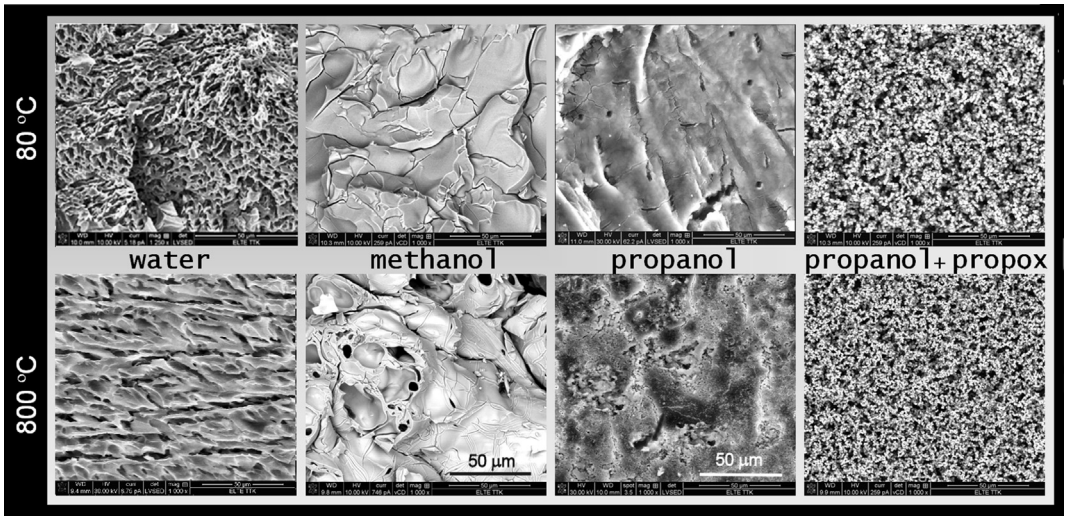

Fig. 1. SEM images of cryogels derived from wet gels swollen in different solvents (1000× magnification).

preparation method yields an optically clear monolith hydrogels. The hydrolysis and the precondensation reactions are performed by refluxing at about 80 °C for 11 h. The organic solvent must be evaporated in order to make the condensation reactions completed. The macroporous foam obtained after the distillation must be swollen by water to obtain a loose hydrogel structure. The aqueous solution turns into a transparent gel after 2–4 h. The second step is the freeze drying of the monolith hydrogel (at 233 K in a Christ, Alpha 2-4 LDplus cryostat instrument). The quality of the swelling solvent (aqueous and alcoholic media) and the drying conditions (pressure: 0.005–0.01 mbar and the rate of freezing: 0.025–2000 °C s^{-1}) have been varied. The molar ratio of water/dried foam has been changed between 10 and 30; the mass ratio 2 and 8. The thickness of the wet gel samples was in the range of 1–2 cm.

2.2. Characterization

The morphology and the pore size and shape of cryogel pellets have been studied by a FEI Quanta 3D FEG *scanning electron microscope* (SEM). The SEM images were prepared by the Everhart–Thornley secondary electron detector (ETD), its ultimate resolution is 1–2 nm. Since the conductance of the particles investigated is high enough to remove the electric charge accumulated on the surface, the SEM images were performed in high vacuum without any coverage on the specimen surface. For the best SEM visibility, the particles were deposited on a HOPG (graphite) substrate surface. SEM combined with energy disperse X-ray spectroscopy (EDX) is mainly applied for spatially resolved chemical analysis of bulk samples. The porosity evaluation has been performed by Amira 5.2.2 software.

In order to visualize the morphology and the inner structure of the created gel, a three-dimensional reconstruction of the cryogel was performed using a dual beam. The dual beam means that besides the electron beam the microscope has a focused ion beam (FIB) as well. The ion beam is suitable for effective slicing and cutting the samples. We created 30 slices in total with 250 nm step size using the high energy Ga^+ ions. The image of every slice was taken by secondary electron detector (ETD). The processing of two-dimensional images was carried out using the Amira 5.2.2 software. The first step of the process was the precise alignment of the slices, which is a key point as it determines the accuracy of the final reconstructed volume. As for the next steps of the reconstruction, the image segmentation and labeling were performed, helping the differentiation and identification of the pore system and the gel body itself. The separation was followed by an interpolation method between the labeled slice, that is intermediate virtual slices were added in order to increase the resolution in the direction of the slicing. Thus, the final slice step size was 9.62 nm. In case of the 3D volume is segmented, the Amira generates a topologically correct polygonal surface model (i.e., with the absence of self-intersections and gaps). Finally, further editing and smoothing

Table 1
Results of the structural investigations of cryogels prepared from hydrogels with various solvent content.

Cryogel samples swollen in	Pore size (µm)		Porosity SEM[a] (%)	TPV[b] ($cm^3\ g^{-1}$)	Spec. Surf. area[c] ($m^2\ g^{-1}$)	Density ($g\ cm^{-3}$)	Thermal conductivity ($W\ (mK)^{-1}$)[d]
	SEM	N_2 sorption					
6× water[e]	10–20 0.008 ± 0.001	10 ± 1	73 ± 15[f]	3.8 ± 0.5	220 ± 50	0.18	0.04–0.044
4× water[e]	10–25 0.008 ± 0.001	8 ± 1	69 ± 15	3.1 ± 0.3	180 ± 50	0.22	0.04–0.045
2× water[e]	2–4 0.007 ± 0.001	2 ± 1	60 ± 10	1.9 ± 0.3	60 ± 30	0.46	0.05–0.06
2× methanol	–	–	5–10	0.045 ± 0.01	26 ± 8	0.84	–
1.5× propanol	2–3	–	57 ± 5	–	–	0.25	–

[a] Macroporosity was determined by SEM images.
[b] Total pore volume.
[c] BET specific surface area was measured by N_2 sorption.
[d] Thermal conductivity data were measured at room temperature.
[e] Mass ratio of water/dried Al-containing gel.
[f] The porosity data is derived from 3D SEM measurements. The cryogels were heated at 80 °C.

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