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Microporous and Mesoporous Materials

Mesopore etching under supercritical conditions − A shortcut to hierarchically porous silica monoliths

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A B S T R A C T

Hierarchically porous silica monoliths are obtained in the two-step Nakanishi process, where formation of a macro−microporous silica gel is followed by widening micropores to mesopores through surface etching. The latter step is carried out through hydrothermal treatment of the gel in alkaline solution and necessitates a lengthy solvent exchange of the aqueous pore fluid before the ripened gel can be dried and calcined into a mechanically stable macro−mesoporous monolith. We show that using an ethanol−water (95.6/4.4, v/v) azeotrope as supercritical fluid for mesopore etching eliminates the solvent exchange, ripening, and drying steps of the classic route and delivers silica monoliths that can withstand fast heating rates for calcination. The proposed shortcut decreases the overall preparation time from ca. one week to ca. one day. Porosity data show that the alkaline conditions for mesopore etching are crucial to obtain crack-free samples with a narrow mesopore size distribution. Physical reconstruction of selected samples by confocal laser scanning microscopy and subsequent morphological analysis confirms that monoliths prepared via the proposed shortcut possess the high homogeneity of silica skeleton and macropore space that is desirable in adsorbents for flow-through applications.

1. Introduction

Silica monoliths with interskeleton macropores and intraskeleton mesopores can be prepared by sol−gel processing combined with phase separation and soft templating strategies relying on various structure-directing agents [1]. Many parameters can be addressed to influence the phase separation through spinodal decomposition during the sol−gel process: from the structure-directing agent chosen as porogen (poor solvents, surfactants, block copolymers, emulsions) over pH and temperature of the starting solution to type and concentration of the silica precursor. These parameters, which affect the progress of phase separation vs. gelation, influence the morphology of the resulting bi-continuous gel, including the degree of macroscopic separation between silica-rich and solvent-rich phase [2−4]. The chemical surface properties of the monolith can be tailored through selecting suitable precursors (co-condensation) or through postsynthesis grafting of functional moieties [5−9].

Following seminal work from the early 1990s [10], Nakanishi and co-workers established a two-step route to macro-−mesoporous silica monoliths in which macropore size and volume can be adjusted largely independent from the skeleton thickness and mesopore size [11,12]. Translated into mass-transport relevant terms, the Nakanishi process offers the possibility to adjust the hydraulic permeability (realized by the flow-through macropores) independently from the surface area (realized by the mesopores) and intraskeleton mass transfer resistance (determined by the skeleton thickness) of hierarchically porous silica monoliths [13], which makes them attractive adsorbents for chemical separations [14,15] and solid−liquid catalysis [16,17]. Their performance in these processes, and hence the overall process efficiency, profits from a high degree of morphological homogeneity, that is, a narrow distribution of pore size and skeleton thickness [18,19]. These attributes are also advantageous when silica monoliths are used as nanocasting templates [20−22], because the morphological quality of the template limits that of the casted porous medium.

The Nakanishi process starts with a silicon alkoxide and an organic polymer, for example, tetramethoxysilane (TMOS) and

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poly(ethylene glycol) (PEG), in acidic aqueous solution [3]. The sol–gel process yields a macro–microporous gel, which is then submitted to hydrothermal treatment (80–120 °C) under alkaline conditions. The micropores in the gel are widened to mesopores through surface etching with ammonia solution, usually generated in situ through thermal decomposition of urea. Urea can already be added to the reactants for the sol–gel step to ensure a homogeneous distribution in the gel before surface etching takes place [23]. After hydrothermal treatment, the aqueous pore liquid is exchanged for methanol to prevent cracking of the fragile gels during the final calcination step. The gel is immersed for 3–5 days in repeatedly refreshed methanol, during which the pore solvent is exchanged and a ripening process occurs in which the siliceous matrix stiffens and shrinks. The ripened gel is calcined at typically 330–550 °C, during which the structure is dried, residual template removed from the pores (by thermal decomposition of PEG), and condensation of the silica backbone completed. Calcination is approached with a shallow heating ramp (i.e., slowly) to avoid the build-up of capillary stress that would crack the monolithic structure. From starting sol to finished monolith, the Nakanishi process takes about one week, whereby most of the preparation time is taken up by waiting for slow processes to complete (Scheme 1).

The time-limiting step in the Nakanishi process is solvent exchange. The same problem has turned up earlier in aerogel fabrication, where supercritical extraction (SCE), which avoids the build-up of capillary stress due to the absence of liquid–gas interfaces, has long been used as an efficient, quick, and mild method for drying [24,25]. SCE drying, however, involves exchanging the pore fluid present after gelation for a suitable SCE solvent (CO_2 or a low alcohol). For fast aerogel fabrication, the dreaded solvent exchange was circumvented by carrying out the whole synthesis (gelation, aging, drying) under supercritical conditions or by choosing a gelation solvent also suitable for SCE drying. Recent examples of fast (5–6 h) aerogel syntheses include a one-step, reactant-to-aerogel route using supercritical methanol [26] as well as a route where an ethanol–water azeotrope served as gelation and as supercritical drying solvent [27,28].

Although an established drying method for aerogels, SCE has not been employed in the preparation of hierarchically porous silica monoliths, except to prevent cracking under special circumstances. Nakanishi and co-workers [29] used the mild conditions of SCE with CO_2 ("cold drying" at 31 °C) to obtain exceptionally large silica monoliths (1.1-L volume) with average mesopore diameters ≤30 nm. While cold SCE drying prevents cracking, it does not reduce the preparation time, because the low miscibility of water and liquid CO_2 requires two complete solvent exchanges: from aqueous pore liquid to methanol to liquid CO_2.

In this work, we eliminate the solvent exchange step from the Nakanishi process through carrying out mesopore etching under the conditions of SCE drying. For surface etching, we need a supercritical fluid that supports the thermal decomposition of urea. Between the two obvious candidate solvents for this task, ethanol is preferred over methanol, because methanol is toxic and supercritical methanol is not inert towards silica. In aerogel drying with supercritical methanol, for example, an unwanted alkylation of surface OH groups and partial dissolution of the silica structure was observed [25,30]. Because the pores hold water from the sol–gel processing step, the SCE fluid is an ethanol–water azeotrope (95.6/4.4, v/v) with a critical temperature of 265 °C. The main task of the supercritical ethanol–water azeotrope (SCEWA) is to provide the conditions for surface etching and SCE drying, but the high temperature and fast mass transport properties of the supercritical fluid are additionally expected to accelerate all involved processes. We thus propose the SCEWA step (Scheme 1) to speed up mesopore formation and ripening, eliminate solvent exchange, and yield dry monoliths that can withstand fast calcination.

2. Experimental

2.1. Chemicals

TMOS was purchased from Acros Organics (Geel, Belgium), PEG ($M_n = 10^4$) and urea came from Merck Millipore (Darmstadt, Germany). Acetic acid, glycerol, and octadecyltrimethoxysilane were
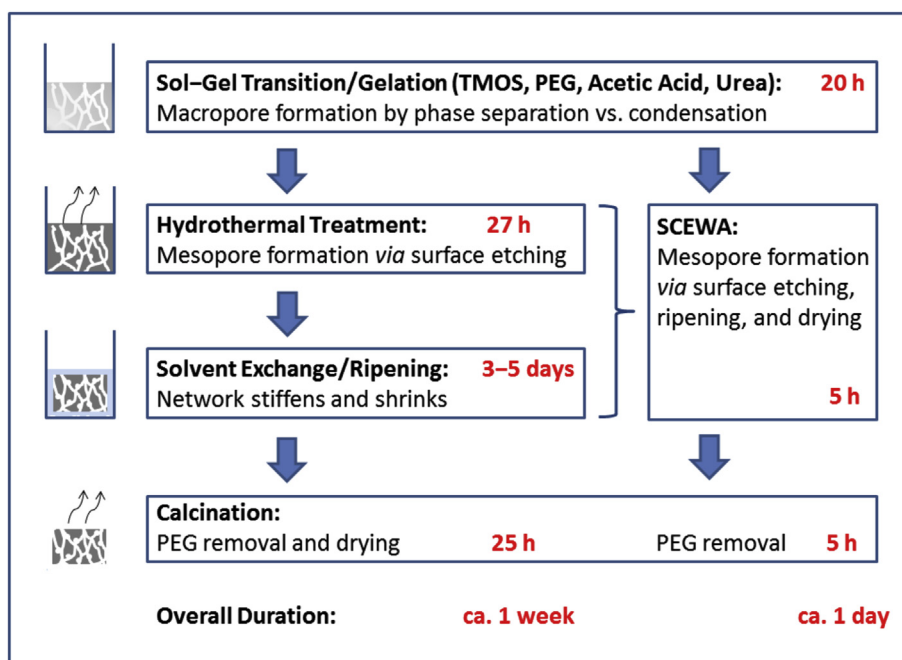
Scheme 1. The classic route to macro–mesoporous silica monoliths via the Nakanishi process (left) vs. the proposed shortcut using a supercritical ethanol–water azeotrope (SCEWA) mixture (right).