



Review

Sulfonated mesoporous carbon and silica-carbon nanocomposites for biomass conversion

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ABSTRACT

Sulfonated mesoporous carbon or silica-carbon nanocomposite materials possess a large amount of accessible SO₃H acid groups, which may have versatile applications as solid acid catalysts in biomass conversion. The mesopores can facilitate the transportation of the large biomass substrates and the targeted products. The hydrophobicity of carbon ensures the hydrothermal stability of the materials, which is essential since biomass conversion usually occurs in polar circumstances (e.g., in water), and it can facilitate the adsorption of reactants and the desorption of formed H₂O during the conversion simultaneously. The other weak acid groups of carbon, like phenolic OH and COOH groups may help the adsorption of reactants or even exert a synergistic catalytic function. With the co-existence of silica phase, the mesopores can be maintained under harsh conditions, e.g., during the sulfonation synthesis step in concentrated H₂SO₄ at a high temperature. Furthermore, the hybrid silica-carbon surface can provide specific polarity from the synergy of both kinds of components and offer potentiality for multi-functionalization. Herein, the synthesis and fabrication of such sulfonated mesoporous carbon and silica-carbon nanocomposite wherein C–SO₃H is confined in mesoporous channels is reviewed. Their state-of-the-art use in catalytic biomass-related conversion such as fatty acids esterification, carbohydrates conversion and furan-derivative condensation, are discussed in detail. The stability issues of the sulfonated carbon or silica-carbon nanocomposites for the specific catalytic reactions are specifically addressed. Finally, a general conclusion is drawn from the above and a future outlook for this class of upcoming materials in terms of synthetic challenges and catalytic application is presented.

1. Ordered mesoporous structure (OMS)

Since the first discovery of mesoporous silica, hexagonally ordered MCM-41 in 1992 by Mobil group, well-ordered mesoporous materials characterized by a precise periodic arrangement of mono-sized pores have stimulated intensive research interests [1–3]. They exhibit large uniform mesopores (from 2 to 50 nm in pore diameter), surface areas and pore volumes that underline their significant applications in various fields, such as catalysis [2,4–11] adsorption [12,13], energy storage [14,15], drug delivery [16,17], sensors [18,19], etc. Besides the mesoporous silica family which mainly includes M41S family [2] and SBA series [3], there have been considerable efforts to incorporate an organic component for an “active” pore surface for easy modification or functionalization, i.e., organic-inorganic hybrid framework [5,16,20–25], or fabricate ordered mesoporous polymers and carbons [7,14,26–31]. These mesoporous silica-carbon nanocomposites -

nanohybrids will be used when the two different building blocks are covalently bonded [20] - and mesoporous carbons hold many attractive features, such as the surface hydrophobicity, high corrosion resistance, as well as good thermal and mechanical stability [21–24,32], in addition to the mesoporous structures. Ordered mesoporous carbon or silica-carbon nanocomposite can be intentionally synthesized with the assistance of structure-directing agents (SDA) or templates, either by the hard-template method using porous solid-state templates as sacrificial or supporting scaffolds or by the soft-template method employing amphiphilic block copolymers as structure-directing agents.

1.1. Hard templating

Hard-templating method is also known as “nano-casting” [28,33–36], which includes the infiltration of nanochannels of a rigid inorganic solid with an appropriate carbon precursor, followed by

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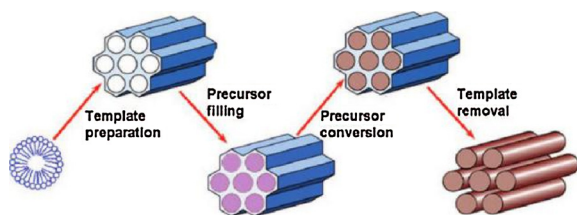


Fig. 1. Schematic illustration for the nanocasting strategy. Reproduced with permission from Ref. [26]. Copyright 2008 American Chemical Society.

further carbonization into the desired materials, as schematically illustrated in Fig. 1. The removal (or not) of the hard-template depends on the porosity of the resultant carbon, whose framework should be not collapsed after the removal of template, and upon applying of the material [37]. The pores can be partly filled (coated) with carbon to form hard-templated silica-carbon nanocomposites, which gives high catalytic performance for esterification of oleic acid [38,39], ethanolysis of 5-hydroxymethylfurfural (HMF) [40], dimerization of α -methylstyrene [41], etc. They also showed a high separation factor with high sorption capacities in the separation of linear from branched alkanes [42]. Compared to carbonaceous materials, silica-carbon nanocomposites possess improved thermal and mechanical stability [43,44], and a higher proportion of stronger acid sites can be created after sulfonation [41,45].

Ordered mesoporous carbon was firstly synthesized by Ryoo's group [33] and Hyeon's group [36] in 1999 by condensing sucrose into carbon under the catalysis of H_2SO_4 inside the mesopores of MCM-48 (CMK-1) and by converting phenol-formaldehyde inside the mesopores of Al-MCM-48 (SNU-1) respectively. After removal by acid [36] or base [33] etching process, ordered mesoporous carbon was retrieved from the silica-carbon composite. Various carbon precursors besides sucrose and phenolic resin have been applied today in the hard template synthesis, such as glucose [41,46], glycerol [47], furfuryl alcohol [42,48,49], 2,3-dihydroxynaphthalene [38,50], *p*-toluenesulfonic acid [40], thiophene [51], pyrrole [51], aniline [52], ionic liquids [53], chloromethylstyrene [54], etc. Most of the carbon precursors can be condensed into carbon phase upon thermal treatment, but in order to avoid random incorporation, initiator such as azoisobutyronitrile (AIBN) [54,55] was also applied to realize a controllable polymerization inside the porous hard template. The hard-templates include MCM-41 [35,42,48], SBA-15 [38–41,46,47,49–55], KIT-6 [38,51], mesocellular silica [38,40], etc. The surface of the hard templates can also be functionalized to serve simultaneously as a catalyst for the carbonization of carbon precursors. For example, SBA-15 was coated with Fe [56] or MCM-41 was treated with $AlCl_3$ [35] to promote the carbonization of phenolic resins, while mesoporous silica-initiator nanospheres [57] were fabricated to realize surface confined atom transfer radical polymerization (ATRP) of methacrylate monomers.

The hard template method corresponds to the grafting strategy (post synthesis) in the synthesis of organosilica (silica-carbon nanohybrid) [5,8,22,25], in contrast to the one-pot co-condensation through self-assembling micellar routes (direct synthesis). The mesoporous silica surface is modified with organic groups through silylation reactions occurring on silanol groups using trichloro-, trialkoxyorganosilane or silylamines as the organic precursors [5]. For example, vinyl-grafted MCM-41 sample was obtained by refluxing MCM-41 in a vinyl-trichlorosilane-containing toluene solution [58].

Although the hard template method has been widely applied and successfully retained or replicated the mesoporous structure, this method has the significant drawback that scale-up for industrial applications is highly difficult, due to the complicated and time-consuming synthesis and the comparatively high cost of using the preformed mesoporous silica as a scaffold. Besides, as an exo-template method is used, the template needs to be wetted by the precursor

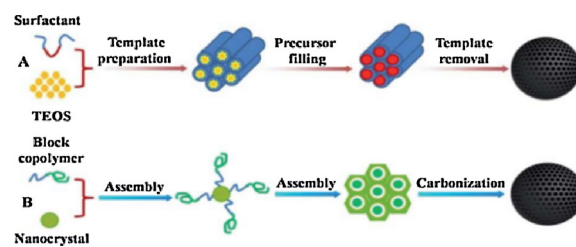


Fig. 2. Schematic illustrations of (A) a hard-template method and (B) a soft-template method for the synthesis of ordered mesoporous carbon. Reproduced with permission from Ref. [31]. Copyright 2015 Royal Society of Chemistry.

molecules, and thus suffers from a random distribution of the carbon constituent, pore blockage, phase separation and a disordered pore architecture [20,27]. Some relatively cheap hard templates, like silica gel (K100) [59], fumed SiO_2 [45] and alumina membrane [60] were applied instead of ordered mesoporous silica, and then only microporosity and/or macroporosity were obtained.

1.2. Soft templating

The soft template method which employs self-assembled structures composed of soft organic materials, has emerged as an alternative to overcome the limitations of the hard template method. As shown in Fig. 2, the key point of the soft-templating route lies in endo-templating, that is the direct use of the self-assembly of the surfactant polymer as the structure-directing agent (SDA), which makes the synthesis simpler and more scalable. Typical soft templates include block copolymers like poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (Pluronic F127 PEO₁₀₆-PPO₇₀-PEO₁₀₆ and Pluronic P123 PEO₂₀-PPO₇₀-PEO₂₀) [61,62] and polystyrene-*block*-poly(4-vinylpyridine) (PS-P4VP) [63]. The structure-directing agent in the soft-template synthesis of mesostructured silica materials can be employed as a carbon source at the same time, with the aid of H_2SO_4 [64,65] or using the thermosetting nature of the surfactant (PEO-*b*-PS) [66]. The mostly adopted carbon precursor for the soft-template synthesis for mesoporous carbon or silica-carbon nanocomposite is phenolic resins and their derivatives [27,31,67]. Later, the application of sucrose as a non-toxic and economical carbon substituent was suggested [68].

There are two main pathways in the soft template synthesis of ordered mesoporous material, namely, cooperative self-assembly (CSA) and liquid-crystal templating (LCT), as shown in Fig. 3 [72]. In the CSA mechanism, the cooperative organization of the already added precursor species and the surfactants molecules occurs to form a mesostructured lyotropic liquid-crystalline phase. The liquid-crystal phase can be developed at lower concentrations of surfactant according to the CSA mechanism. This mechanism was later proven by *in situ* Small Angle X-ray or Neutron Scattering (SAXS or SANS) in the sol-gel synthesis of mesoporous silica materials, as the hybrid silica-surfactant micellar aggregates prior to the precipitation of the material were detected [70]. In the LCT mechanism, the surfactant molecules organize into true or semi-liquid crystal mesophase micelles after reaching the critical micelle concentration (CMC) and the formed lyotropic liquid crystalline phase serves as a template for the incorporation of precursors for the formation of the mesostructure. The versatile evaporation induced self-assembly (EISA) can be assigned to this mechanism, as the highly concentrated surfactants form liquid-crystal phases in the presence of precursors during the final stage of solvent evaporation [69,71].

For the soft template synthesis of ordered mesoporous silica, there are many self-assembly driving forces under different pH conditions [2], such as I^-S^+ , $I^+X^-S^+$, I^+S^- , where I is inorganic precursor, S is surfactant and X^- is the anion. However, for the direct organization of surfactant and organic precursor, mainly self-assembly induced by

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