Preparation of composite carbon–zeolite membranes using a simple method

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Zeolite thin films and composites supported on different materials have been widely used as highly selective membrane separators, membrane reactors, chemical sensors, and microdevices [1–11]. In particular, zeolite membranes supported on polymers and ceramics as supports are universally studied. However, polymers are vulnerable to organic solvents and could not tolerate high temperatures. Ceramics provide better mechanical strength and thermal stability, but are more difficult to fabricate and therefore are more expensive. Moreover, ceramics also have a little etching of aluminum by a strong alkaline solution [1]. Porous carbon materials are promising candidates as supports for zeolite membranes because they not only possess comparable mechanical strength, thermal characteristics of metallic supports, and excellent resistance to chemical attack, but also exhibit organic substrate's flexibility of forms and lower capital cost [10, 11, 12]. Zeolite films grown on porous carbon materials can modify the nature of the porous carbon itself and present different potential advantages in a number of applications. On the other hand, the pores of porous carbon materials can be narrowed down to a desired uniform subnanometer size by the zeolite growth on the porous carbon surface, which is one of the most difficult but a fascinating task that carbon researchers have to attempt [12]. The main difficulty is that there are few nucleation centers on the hydrophobic carbon supports, which make it difficult for zeolites to nucleate and grow on them from the hydrophilic zeolite synthesis solution. Up to now, there are few studies on the growth of zeolites on the activated carbon and hollow fibers as supports by using the oxidizing pretreatment of the carbon materials to increase the oxygen functional groups and the surface change in the carbon materials with a cationic polymer for the zeolite growth [11, 13–15]. Recently, continuous zeolite/carbon composites are obtained by electrophoretic deposition of zeolite nanocrystals on porous carbon disks, then followed by hydrothermal synthesis [16]. In this communication, we report a simple and effective method for preparation of continuous carbon-silicalite-1 membranes on porous carbon tubes.

A 1%wt zeolite silicalite-1 colloidal suspension in ethanol prepared from the recipes described by Yeung and coworkers [9]. Porous carbon tubes prepared at Dalian University of Technology have 9 mm OD, 5 mm ID, 75 mm long, and a nominal pore size of 0.3 μm. Prior to use, the tubes were rinsed with DDI water and then dried at 393 K for 10 hr. A thin layer of zeolite seeds was coated onto the inner surface of the tubes using a slip-casting technique in 1wt% seed suspension for 30 s contact time. The seeded supports were dried at room temperature overnight and calcined in air at 523 K for 6 hr. After calcination, the seeded tubes were immersed vertically in the clear synthesis solution with a molar composition of $20SiO_2$:2.5 $(TPA)_2O$:10 000H_2O at 403 K for 36 hr. After the synthesis, the sample was characterized by scanning electron microscopy (SEM, JEOL JSM-6300F) and X-ray powder diffraction (XRD, Philips PW 1030).

Fig. 1 is the SEM images of the prepared carbon–zeolite composites. Without seeding, no zeolite film is formed on the untreated carbon support except for the very few crystal deposits (Fig. 1a). This reflects that the carbon surface is extremely inert and zeolites are unable to grow on the untreated carbon support. It is clear from Fig. 1b that after the support is seeded by using slip-casting in seed ethanol suspension, the seeds are successfully introduced onto the carbon surface. The carbon surface is fully covered with 5 μm thick layer of silicalite-1 seeds. This not only makes the carbon surface even and smooth, but also provides anchoring centers for zeolite growth, which both favors forming a continuous and dense membrane on the carbon support. After hydrothermal synthesis, a continuous zeolite membrane of 5–6 μm thickness is formed on this seeded support as shown in Fig. 1c. The zeolite crystals grow outward from the surface of the seed layer. From the surface (Fig. 1c inset), the zeolite membrane is well intergrown and possesses a smooth and uniform surface. Under the conditions of 1 bar and room temperature, the membrane shows no N_2 permeation. This fully proves that the carbon–zeolite membrane is dense and perfect. XRD patterns of the samples in Fig. 2 show that both the seeded carbon support and the membrane have strong characteristic peaks with a silicalite-1 structure [17], but with different relative peak intensities. This confirms the existence of a seed layer on the support and the formation of the silicalite-1 zeolite layer on the seeded support.

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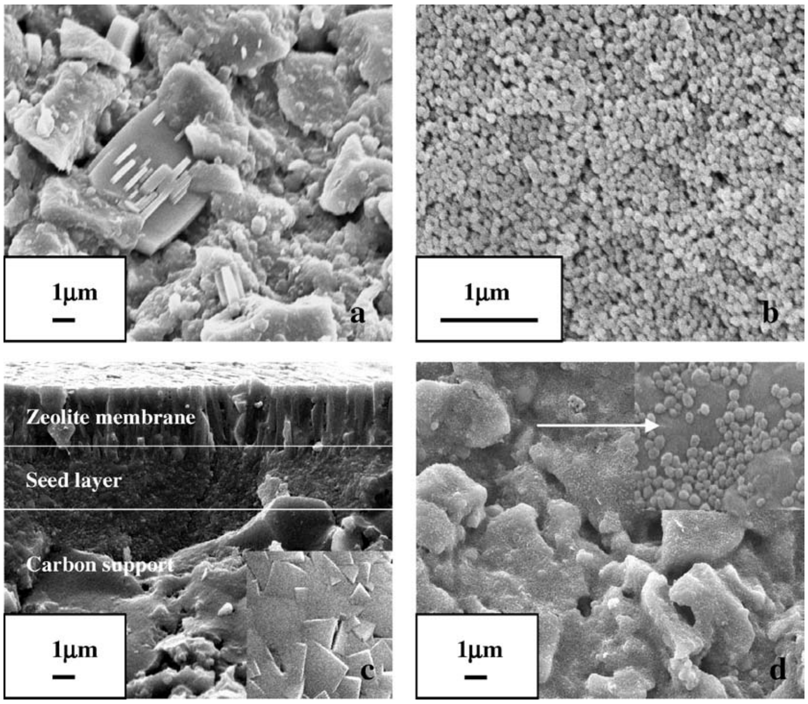

Figure 1 SEM images of the seeded supports and the grown composites; (a) surface section of the grown composite on the unseeded support; (b) surface section of the support seeded in 1%wt seed ethanol suspension for 30 s; (c) surface and cross sections of the grown composite on the support seeded in 1%wt seed ethanol suspension for 30 s; (d) surface section of the support seeded in 1%wt seed water suspension for 30 s.

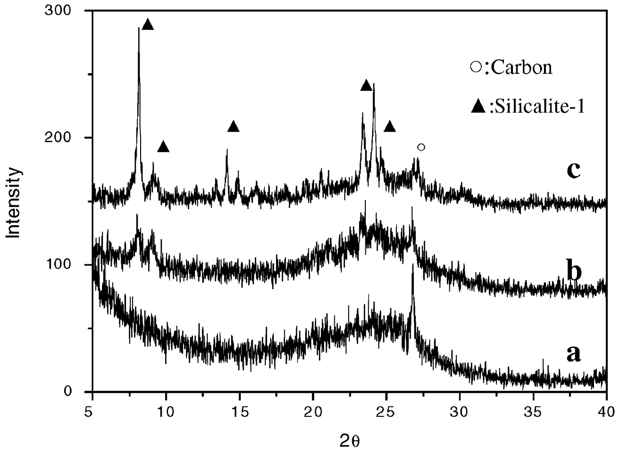

Figure 2 XRD patterns of (a) the carbon support, (b) the seeded support and (c) the regrown silicalite-1 zeolite membrane on the seeded support.

It is worth noting that the result of the seeding from the seed water solution is greatly different from that from the seed ethanol solution. A continuous seed layer on the carbon support can be formed from the seed ethanol suspension, whereas no seed layer is obtained except for few seeds from the seed water suspension for the same contact time (Fig. 1c and inset). The support still has a coarse and uneven surface. In fact, a seed layer can be easily formed on a porous ceramic support by using the slip-casting technique from a nanoseed water suspension [18]. It is implied that the seeding solvent plays a key role in the formation of a seed layer on the carbon support for the slip-casting method. This may be mainly attributed to the wettability of the support in different solutions, which produces different capillary action. When the porous support is dipped in the seed suspension, the dispersion medium is forced into the pore of the support by capillary action of the porous support. At the interface the seeds are retained and concentrated at the entrance of pores to form a seed layer. The better the wettability of the support is, the stronger is the capillary action of the support [19]. The strong hydrophobic carbon support presents better wettability in seed ethanol suspension of weaker polarity, whereas it has worse wettability in seed water solution of stronger polarity.

In conclusion, a simple and effective method for successfully preparing a composite carbon–zeolite silicalite-1 membrane has been developed. The method involves two-step procedures in which nanoseeds for the regrowth of zeolites were introduced to the supports by using a seeding technique in seed ethanol suspension and then grown into continuous films by hydrothermal treatment. This method enables crystallization of continuous zeolite films on supports with very inert chemical reactivity and is also suitable for preparing other types of composite-zeolite membranes by modifying seed types, synthesis solution, and conditions. This opens up routes for the preparation of carbon–zeolite films on porous carbon materials. The composite-zeolite membranes obtained using this method can greatly improve the surface properties and pore sizes of carbon supports and may have potential applications in catalysis and separation.

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