Carbon-Zeolite NaA Composite Membranes

Xiongfu Zhang,[1] Haiou Liu[1], King Lun Yeung[2], Jinqu Wang[1]*

[1]Institute of Adsorp. and Inorg. Membr., School of Chem. Eng., Dalian University
of Technology, No.158 Zhongshan Road, Dalian 116012, P. R. China.
E-mail: *xfzhang@dlut.edu.cn*; *membrane@chem.dlut.edu.cn*

[2]Department of Chemical Engineering, the Hong Kong University of Science and
Technology, Clear Water Bay, Kowloon, Hong Kong, SAR-PR China

1. Introduction

Zeolites are crystalline microporous materials with well-defined and uniform pore structure that find extensive industrial uses as adsorbents, catalysts and ion exchangers [1-2]. Zeolite films supported on different materials have been successfully prepared and have potential applications as highly selective membrane separators, membrane reactors, chemical sensor and microdevices [3-10]. Most of the early work focused on zeolite membranes grown on polymers and ceramics as supports. Porous carbon materials are promising candidates as supports because of their high internal surface area, porosity and excellent stability in a non-oxidising atmosphere. Zeolite films grown on porous carbon supports can modify the nature of the carbon materials themselves and present different other types of potential advantages in a number of applications. On the other hand, by being grown with a layer of zeolite, the pores of porous carbon materials can be narrowed to a desired uniform subnanometer size, which is one of the most difficult but fascinating tasks that carbon researchers have to attempt [11]. This may open up a novel approach to tune the pore structure of porous carbon materials at a subnanometer level by changing the size or the shape. This work investigates the preparation of zeolite NaA membranes on porous carbon tubes.

2. Experimental

2.1. Materials

The porous carbon tubes prepared by Dalian University of Technology have 9 mm OD, 5 mm ID and a nominal pore size of 0.5 µm. The chemicals used for zeolite seed and membrane synthesis include tetraethyl orthosilicate (TEOS, 98 %), sodium aluminate (Al_2O_3 54 wt.%, Na_2O 41 wt.%), Ludox SM-30 (SiO_2 30 wt.%) that were supplied by Aldrich Chemicals. Sodium hydroxide (>98%), tetramethylammonium hydroxide ($TMAOH\cdot 5H_2O$, 98.5%) and ethanol (99.8%) that were supplied by home-made Chemicals.

2.2 Preparation of the supports, seeding and membranes

Zeolite NaA seed of ~150nm was prepared according to the previous report [9]. Prior to use, the carbon supports were rinsed with DDI water and then dried at 120°C for 10 h. A thin layer of zeolite seeds was coated onto the inner surface of the tubes using a slip-casting in 1wt % seed ethanol solution for 30s contact time. The seeded supports were dried at room temperature overnight and calcined in air at 523K for 6h at 1 K/min. The seeded tube was wrapped with Teflon tape before it was placed vertically in the clear synthesis solution with a molar composition of $1Al_2O_3 : 5SiO_2 : 48Na_2O : 4500H_2O$. The synthesis solution was prepared by mixing together the desired amounts of sodium aluminate, sodium hydroxide, tetraethyl orthosilicate and water. The aluminosilicate solution was stirred at room temperature for 12 h to obtain a clear and homogeneous solution. This solution was transferred to a Teflon container and the seeded support tubes were immersed in the solution. The Teflon container was sealed in a stainless steel autoclave and placed in a preheated oven of 373 K and allowed to crystallize for the desired time. After the synthesis, the prepared samples were dried at 393K for 10h in an oven. The crystalline structure of the zeolite membrane was analyzed by XRD to identify the type of zeolite formed and the crystallinity of the zeolite layer. The morphology, microstructure and thickness of the zeolite layers were determined by SEM from both the surface and the cross-section.

3. Results and discussion

3.1 Zeolite growth on the untreated carbon support

Fig.1 shows the shape (a) and surface microstructure (b) of the carbon support. Although the carbon support possesses a uniform cylindrical shape, the surface is extremely coarse, uneven and has some large holes. It is difficult to for zeolites to grow on untreated carbon supports by direct conventional hydrothermal synthesis as shown in Fig.1(c). When the untreated support is placed in the synthesis solution for zeolite crystallization at 373 K for 12 hours, except for the few crystal deposits, no zeolite layer is formed on the unseeded support. This may be mainly attributed to few oxygen functional groups on the support, which leads to the bad interaction between the zeolite synthesis solution and the carbon surface [12].

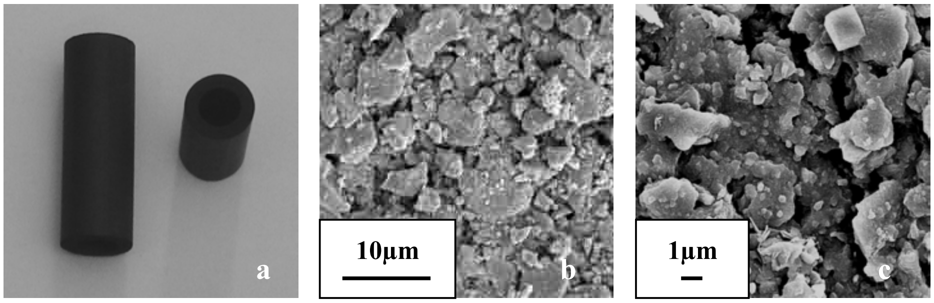

Fig.2 SEM images of the carbon supports (a, b) and grown support without seed (c)

3.2 Seeding and the growth of zeolite membranes on seeded supports

For successful zeolite membrane formation, proper nucleation sites are necessary to allow for preferential nucleation and growth of zeolite crystals on the support surface. Seeding is an effective method for the preparation of zeolite membranes on ceramic supports using a slip-casting method [13]. In the light of this technique, the porous carbon tubes were seeded with NaA seeds of around 150nm. Figure 3 shows the SEM images of the seeded carbon supports from 2 wt% seed water solution for 30s contact time and the zeolite growth on the seeded carbon supports by hydrothermal synthesis at 373K for 12h. It is clear from the Fig.3a that except for the few nanoparticles inside the pores and on the lower part of the support, no seed layer is formed on the seeded support. The surface of the support is still coarse and uneven. XRD pattern from Fig.5a shows that there are also no characteristic peaks of any zeolite NaA seeds on the seeded support. After crystallization, the zeolite membrane with approximately 4μm thickness is formed on the seeded support (Fig.3c), however, the membrane displays a coarse, uneven surface and poorer intergrowth (Fig.3b). It is indicated from Fig.5b that there are characteristic peaks of NaA zeolite. This is in agreement with the SEM results. It is obvious that there is a progressive improvement in the zeolite growth in comparison with the result of the growth on the unseeded support. These seeds on the support act as good anchorage centers during the synthesis, though there are only a small number of the NaA seeds on the support.

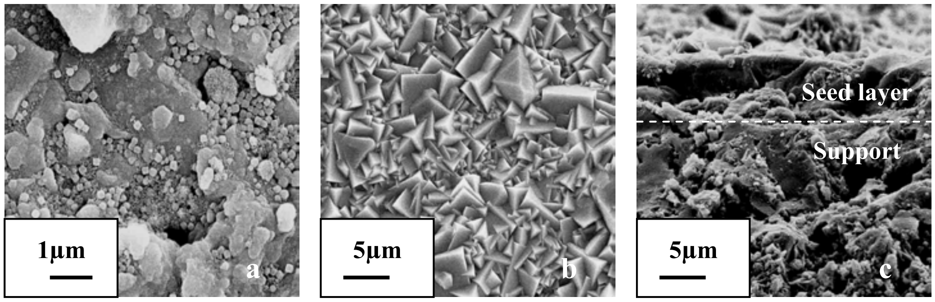

Fig.3 SEM images of the carbon support seeded from 2 wt% seed water solution for 30s (a) and the membrane grown on the seeded carbon support at 100°C for 12h (b, c).
(b): Surface; (c): Cross section.

In order to further improve the quality of the seeded support and zeolite membrane formed by the subsequent synthesis, the carbon supports were seeded from 1wt% seed ethanol solution for 30s contact time, followed by hydrothermal treatment from the same synthesis solution and same synthesis conditions. Fig.4 shows the SEM images of the seeded support and the grown membrane. It is clearly indicated that a continuous, uniform and smooth seed layer on the carbon surface is formed (Fig.4a). This uniform seed layer greatly improves the surface property and roughness of the carbon support, which favors the formation of the zeolite membrane with high quality by subsequent hydrothermal synthesis. In fact, it is clearly seen from Fig.4b and 4c that after hydrothermal synthesis, a continuous and dense zeolite membrane is formed. The crystals growing outward from the surface of the seed layer are very uniform and intergrow very well. The thickness of the membrane is about 3 μm and the average thickness of the seed layer is around 4 μm. The intrusion of some seeds into the large voids of the support can also increase the adhesion between the seed layer and the carbon surface. XRD patterns from Fig.5 display the characteristic peaks of NaA zeolite without other types of zeolite peaks for both the seeded support and the grown membrane, but with different relative peak intensities. The intensity of NaA zeolite peaks on the grown membrane is much stronger than that on the seeded support, which reflects the increase of the zeolite thickness and the formation of the continuous membrane. In comparison with the XRD pattern of the support seeded in seed water solution (Fig.5a), the presence of characteristic peaks of NaA zeolite on the support seeded in seed ethanol solution (Fig.5a) fully confirms the formation of the seed layer.

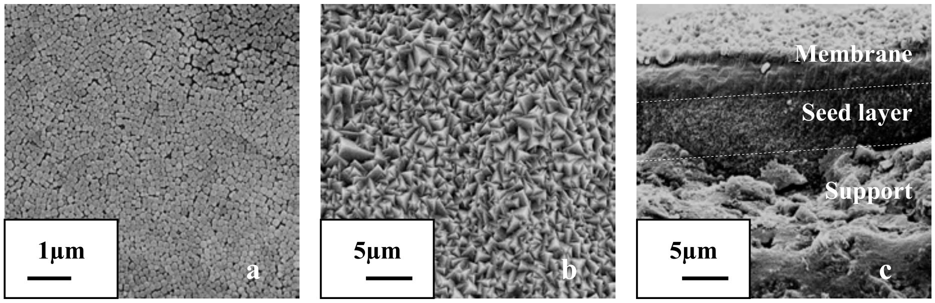

Fig.4 SEM images of the carbon support seeded from 1wt% seed ethanol solution for 30s (a) and the membrane grown on the seeded carbon support at 100°C for 12h (b, c).
(b): Surface view; (c): Cross section.

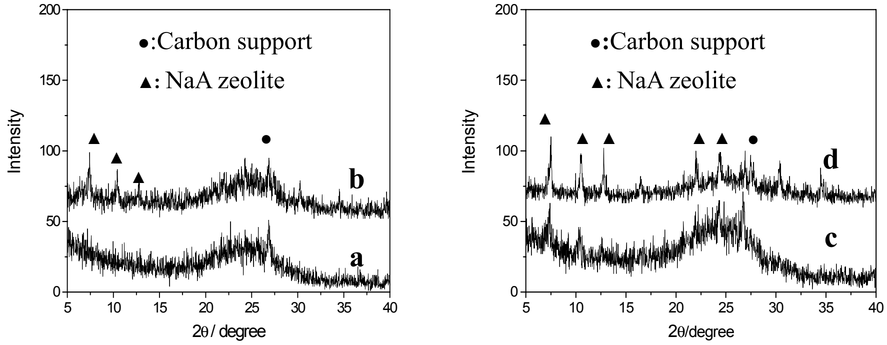

Fig.5 XRD patterns of the seeded support and the grown membrane at 100°C for 12h
a, b: Support seeded from 2% seed water solution and grown membrane, respectively
c, d: Support seeded from 1% seed ethanol solution and grown membrane, respectively

3. Conclusions

Carbon-zeolite NaA composite membranes have been successfully prepared on porous carbon tubes by a simple and effective method involving seeding and regrowth. Seeding solvent has an important influence on the deposition of seeds on porous carbon material. A continuous seed layer was formed by slip-casting technique in seed ethanol suspension and a dense and well-intergrown carbon-NaA zeolite membrane was then obtained on the seeded tube by hydrothermal synthesis. The continuous seed layer formed ensures effective zeolite nucleation and growth, which enables crystallization of continuous zeolite membranes on the seeded carbon supports by subsequent hydrothermal synthesis. This synthesis method may be suitable for the preparation of other types of composite-zeolite membranes by modifying seed types, synthesis solution and conditions and also opens up a novel route for tailoring and improving carbon pore structure of porous carbon materials.

Acknowledgments

We are grateful for the financial support by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the Dalian University of Technology (1000-893305).

References

[1] Davis M E. Nature 2002; 17:813-821.
[2]Szostak R. in:Molecular Sieves, second ed., Blackie Academic & Professional, London, 1998；.
[3] Lai Z, Bonilla G., Diaz I, , et al. 2003; 300: 456-460.
[4] Tavolaro A., Drioli E. Adv Mater 1999; 11: 975-996.
[5] Iwasaki A, Sano T, Kiyozumi Y. Micropor Mesopor Mater 2001; 38:75-83.
[6] Mintova S, Mo SY, Bein T. Chem Mater 2001; 13:901-905.
[7] Chau J L H, Yeung K L. Chem Commun 2002; 13:960-961.
[8] Xiongfu Zhang, Tonghua Wang, Haiou Liu, et al. J. Mater. Sci. 2004; 39:5603-5605.
[9] Xiongfu Zhang, Wenqin Zhu, Haiou Liu, et al. Mater. Letters. 2004; 58:2223-2226.
[10]Valtchev V, Hedlund J, Schoeman B J, et al. Micropor Mater 1997; 8: 93-101.
[11] Kyotani T. Control of pore structure in carbon. Carbon 2000; 38: 269-286.
[12]García-Martínez J, Cazorla-Amorós D, Linares-Solano A, Lin YS. Micropor Mesopor Mater 2001; 42: 255-268.
[13] Lovallo M C, Gouzinis A, Tsapatsis M. AIChE J 1998; 44:1903-1913.