

A novel carbon/ZSM-5 nanocomposite membrane with high performance for oxygen/nitrogen separation†

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A novel carbon/ZSM-5 nanocomposite membrane is successfully prepared by incorporating nano-sized ZSM-5 into polymeric precursor (polyimide), which shows excellent permselectivities for separation of oxygen/nitrogen gas pairs.

Separation of air into oxygen and nitrogen is an important process, which is currently practised primarily by energy-intensive cryogenic distillation and pressure swing adsorption techniques. In addition to these traditional approaches, the separation technique based on membranes has also been actively pursued, to which the key is the membrane materials with desired properties such as well-tuned pore structure. Carbon membranes have ultramicropore structure with nominal pore diameters of 3–5 Å, which are close to the diameters of O₂ and N₂ (O₂: 3.8 Å × 2.8 Å; N₂: 4.2 Å × 3.2 Å), and thus they could be good candidates for air separation if the membrane structures can be tailored to separate O₂ and N₂ efficiently.¹ For carbon membranes, the structure characteristics and gas separation performance mainly depends on the organic precursor and heat treatment process adopted. To date, many types of polymers have been tested as the precursor of carbon membranes such as poly(furfuryl alcohol),^{2–4} poly(vinylidene chloride),⁵ phenolic resins,^{6,7} polypyrrolone,⁸ coal tar pitch,⁹ polyimide (PI)^{10–28} and polyimide containing siloxane.^{29–31} Though great progress has been made in the field of carbon membranes, it is not uncommon that a strong trade-off relationship exists between the permeability and the selectivity, *i.e.* the permeation flux through the carbon membranes is considerably reduced as the gas selectivity increases because of the disordered pore structure and diffusion resistance in membranes. To tackle this challenging issue, some strategies such as the synthesis of composite membranes by incorporation of silica have been envisaged,³² but it is still far from satisfactory.

To solve the challenging task mentioned above, here we propose a simple strategy that could substantially improve the gas flux without losing the selectivity of membranes. Specifically, we prepared carbon/ZSM-5 composite membranes by incorporating nano-sized ZSM-5 into the polymeric precursor (polyimide) and

subsequently heated the composites at 873 K under an argon atmosphere. The as-prepared composite membranes are composed of continuous carbon matrix and a dispersed zeolite ZSM-5 domain with ultra-uniform micropores. Below is the motivation for us to incorporate nano-sized ZSM-5 as filler in carbon membranes. Firstly, zeolite ZSM-5 features periodic arrays of uniform pores (~0.55 nm) and can endure high temperature treatment, thus, its structure is not easily destroyed during the pyrolysis, and the pores in the zeolite will remain intact to some degree and function as continuous transport pathways for gas molecules, which would help to minimize the resistance in the gas diffusion process. Secondly, the nano-sized particles of zeolite may help to create interfacial gaps between carbon phase and nano-zeolite because of the phase separation effect, which may help to increase the permeability of gas molecules through the membrane. Finally, since zeolite particles are embedded in the carbon matrix, the pore windows of ZSM-5 may be modified to some degree by carbon formed *in situ* during the pyrolysis process, which also could help to improve the selectivity of the composite membranes. In comparison to ZSM-5 molecular sieves, zeolite 4 A without any treatment is a suitable candidate for air separation owing to its pore size (0.41 nm),^{33–35} however its structure is not steady enough, which makes the permselectivity of O₂/N₂ decrease under higher temperature treatment.³⁶ Therefore, zeolite 4 A is not an appropriate molecular sieve to be incorporated into the nano-composite carbon membranes in the present work.

Below is the detailed description about the process for making carbon/ZSM-5 composite membranes with continuous carbon matrix and dispersed ZSM-5 zeolite. The nano-sized ZSM-5 used was synthesized according to the method reported by Van Grieken *et al.*³⁷ For a typical run, chemicals with a molar composition of 9 TPAOH : 0.16 NaOH : 1 Al₂O₃ : 25 SiO₂ : 500 H₂O : 100 EtOH were mixed and stirred at room temperature overnight to ensure TEOS and aluminium isopropoxide undergo hydrolysis into ethanol and isopropyl alcohol, respectively. Then, the solution was heated at 353 K to get rid of water and alcohols, yielding a concentrated solution that was subsequently transferred into a teflon-lined stainless-steel autoclave, and crystallized by thermal treatment under autogenous pressure and static conditions at 443 K for 120 h. After this treatment, a solid product was obtained and separated by centrifugation, washed several times with distilled water, dried overnight at 393 K and calcined in air at 873 K for 6 h. Fig. 1 shows the TEM images of the solid products that actually are nanocrystals with a particle size ranging from 20 nm to 50 nm.

The as-obtained dry zeolite ZSM-5 was dispersed in *N,N*-dimethylacetamide (DMAC) under stirring and ultrasonic treatment for 2 h, leading to a suspension that was mixed with

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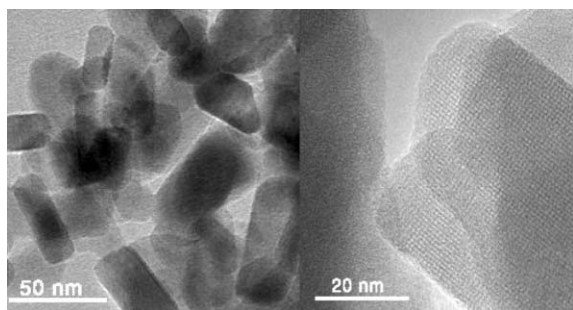


Fig. 1 Typical TEM images of ZSM-5 nanocrystals.

poly(amic acid) (PAA) solution (30 wt.%) derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA). The content of the nano-sized ZSM-5 in the PI (polyimide)/ZSM-5 matrixes was controlled to be 4.8 wt% (denoted PIZ1), 9.1 wt% (denoted PIZ2), and 16.7 wt% (denoted PIZ3). Following a prepolymerization step at 298 K for 10 h, a homogeneous solution was cast on a glass plate and dried at 313 K for 12 h. The resulting PAA/ZSM-5 composite membranes were heated at 373 K, 473 K, and 623 K in flowing argon for 1 h in each step. Then carbon/ZSM-5 membranes with a thickness of 50–60 μm were pyrolysed at 873 K for 2 h in flowing argon of 100 ml min^{-1} at 2 K min^{-1} .

Fig. 2 shows typical HRTEM images of the composite carbon membranes (PIZ2), from which it can be seen that ZSM-5 particles embedded in membranes have ordered channels (see Fig. 2a), while the carbon phase in the membrane has a turbostratic structure with several layers consisting of graphite-like microcrystallites (see Fig. 2b). During the heat treatment process, the abrupt evolution of gases in the early pyrolysis stage has been observed due to the cleavage of the imide ring or C–N bond, which transforms the crystalline state of polyimide to an amorphous state, and the gas released (mainly N_2) in the further pyrolysis steps makes the layers or planes of graphite-like microcrystallites grow further.³⁸ The micro-channels generated in the carbon matrix help to improve the gas selectivity, while the ordered channels in the zeolite may provide pathways for gas molecules to be separated. All the structural changes in the composite membranes combine to considerably influence the gas transport behavior of the nanocomposite carbon membranes, in this case a kind of synergistic effect cannot be ruled out.

Fig. 3 shows the XRD patterns of the carbon membrane derived from polyimide, nano-sized ZSM-5 and composite carbon membranes. For traditional carbon membranes, a broad weak (002) peak is present, which can be attributed to the turbostratic structure with randomly oriented graphitic carbon layers. In the

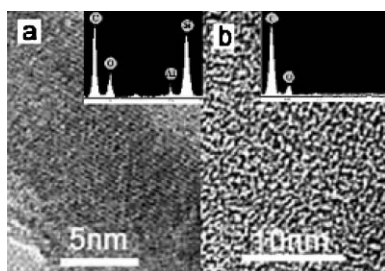


Fig. 2 High-resolution TEM images of composite membranes (PIZ2): (a) ZSM-5 embedded in membranes, (b) carbon phase in membranes.

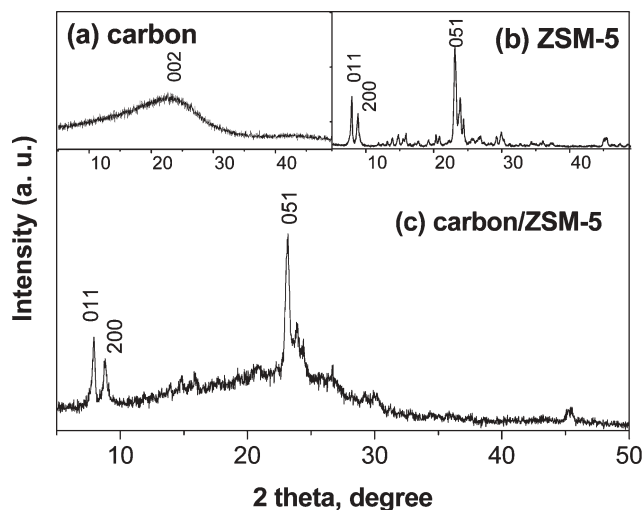


Fig. 3 XRD patterns of normal carbon membranes (a), ZSM-5 (b) and nanocomposite carbon membranes PIZ2 (c).

case of composite carbon membranes (PIZ2), peaks with high-intensity (011), (200), and (051) can be clearly seen, which are indicative of typical ZSM-5 structures, indicating that the structure of the zeolite is not destroyed during the heat treatment step. The XRD study also reveals that no significant changes are observed in the crystal size of the ZSM-5 zeolite before and after being incorporated into the membranes.

Nitrogen adsorption isotherms of carbon composite membranes, measured at 77 K, feature steep uptake at low relative pressure of $P/P_0 < 0.1$ (Fig. 4), showing the intermediate type between types I and II according to the IUPAC classification, which suggests that ultra-micropores are present in the nanocomposite carbon membranes. It is also found that the nanocomposite membranes have a narrow pore-size distribution, which is obtained from the adsorption branches of the isotherms using the Horvath–Kawazoe (HK) method. For the PIZ2 composite membrane (9.1 wt% ZSM-5) with BET surface area of 408 $\text{m}^2 \text{g}^{-1}$ and a total

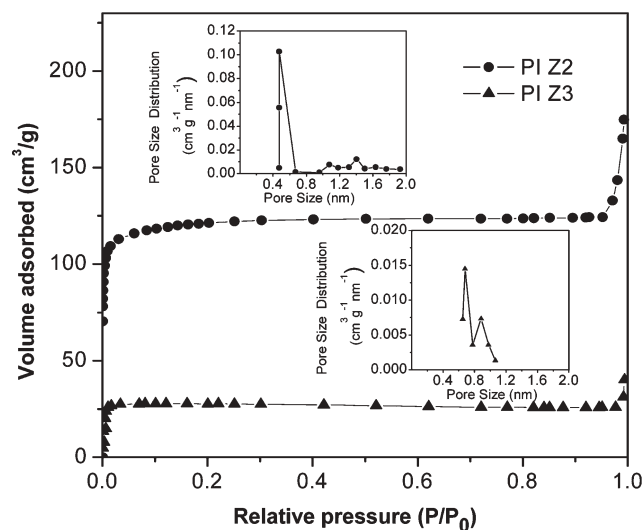


Fig. 4 Nitrogen adsorption isotherms of nanocomposite carbon membranes at 77 K, insert showing pore size distribution calculated by the HK method.

Table 1 Permeation properties of carbon/ZSM-5 membranes at 298 K

Membrane	Flux/Barrers ^a		Selectivity O ₂ /N ₂
	O ₂	N ₂	
PI (polymeric membrane)	0.16	0.04	4.2
PI (carbon membrane)	2.21	0.16	13.8
PIZ1 (4.8 wt% ZSM-5)	70.0	5.85	12
PIZ2 (9.1 wt% ZSM-5)	431.0	30.0	14.4
PIZ3 (16.7 wt% ZSM-5)	499.0	39.6	12.6

^a 1 Barrer = 1 × 10⁻¹⁰ cm³(STP) cm/cm² s cmHg.

pore volume of 0.1691 cm³ g⁻¹, the pore-size distribution centers at 0.47 nm, while for PIZ3 (16.7 wt% ZSM-5) the distribution center shifts to 0.71 nm as the zeolite loading increases. Here it should be noted that for pure carbon membranes, the pore size is ca. 0.4 nm. It has been well established that the separation mechanism of gases on carbon membranes is based on the molecular-sieving effect. The membranes containing constrictions in the carbon matrix may allow the smaller molecules to go through the pores while the larger molecules are blocked out. In the case of nanocomposite carbon membranes, the narrow pore-size distributions imply that the predominant transport mechanism involved may follow the molecular sieving scheme.

Molecular probe studies were conducted at 298 K with a variable volume-constant pressure method to measure the permeability of a single-component gas through the as-obtained membranes. The tested gases included H₂, O₂, and N₂. For each membrane, measurements were conducted 3 times and the reported final results are the averaged ones. The precision or accuracy in permeability measurements is estimated to be within ±10%. Table 1 shows the gas permeability results of the traditional carbon membranes and the nanocomposite carbon membranes with different zeolite loadings that were prepared by pyrolysis at 873 K. It can be seen from Table 1 that the permeability of all gases tested increases significantly at higher zeolite loading in the carbon matrix, indicating that a kind of well-developed ultramicroporous structure is present in the nanocomposite membranes. In addition, the selectivity of the oxygen to nitrogen in the case of composite membranes remains at 12 to 14.4 with an O₂ permeability of 70 to 499 Barrers. Interestingly and strikingly, the trade-off relationship between the permeability and selectivity is not obvious as the zeolite loading increases. It is well known that ZSM-5 is a non-selective porous zeolite with a pore size greater than oxygen and nitrogen, thus the oxygen/nitrogen selectivity should be mainly attributed to carbon matrix in the nanocomposite membranes, and the pore windows of ZSM-5 could be modified by carbon formed during the pyrolysis process, which would also help to improve the selectivity of the nanocomposite membranes. The promising results presented here are encouraging in terms of permeability and selectivity compared with the results of organic membranes and traditional carbon membranes.

In summary, novel carbon/ZSM-5 nanocomposite membranes with well-developed ultramicropores have been successfully prepared by incorporating nano-sized ZSM-5 into polymeric precursor (polyimide). The composite membranes show excellent permselectivities for oxygen/nitrogen gas mixtures in comparison to the traditional carbon membranes and polymeric membranes. It has been demonstrated that it is possible to substantially improve the gas permeability without a significant loss of separation efficiency by simply changing the zeolite content embedded in the

carbon membranes. It is believed that the method reported here could be readily extended to the preparation of other carbon/zeolite composite membranes. These nanocomposite carbon membranes with excellent performance would be of great potential in gas separation.

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