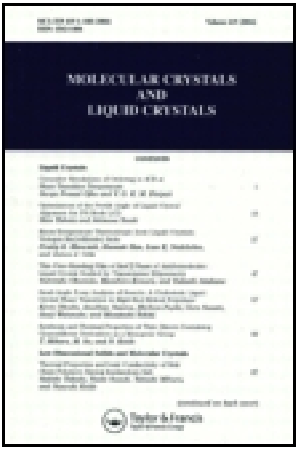

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Gas Permeation Properties of Carbon Molecular Sieve Membranes Prepared in Alkali Metal-Organic Solvent Systems

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Gas Permeation Properties of Carbon Molecular Sieve Membranes Prepared in Alkali Metal-Organic Solvent Systems

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Intercalation of alkali metals into carbon molecular sieve (CMS) membranes was studied to get new materials for gas separation. The preparation was carried out in ether solutions, containing phenanthrene and alkali metal. The mechanical stability was satisfied for potassium doped CMS, prepared in MeTHF. XRD analysis suggested a random stage structure for the modified membrane due to the low crystallinity of the original host carbon. Characterized by time- lag method some increase in the He and N_2 permeability was observed by intercalation, because the graphite- like hexagonal layers were expanded and/or larger pathways were formed, so that the gas molecules could easily diffuse through. One membrane doped with potassium, followed by partial de- intercalation, exhibited an interesting perm- switch behavior at around 323 K.

Keywords: carbon molecular sieve membrane; gas permeation; intercalation; alkali metal

INTRODUCTION

Considerable interests have been directed to develop "high- performance" membranes that can be used for separation and recovery of gases, vapors and value- added products as well as for membrane reactor system (simultaneous separation and catalytic reaction). Carbon molecular sieve (CMS) membrane is one of the favorite candidates for those purposes, because the membrane exhibits excellent gas separation performance that originates in slit- shaped micropores of molecular dimension[1]. However, these CMS membranes hardly use interlayer spacing of graphite-like microcrystallines, leading to rather small permeability and gas-membrane interaction. Future demand of the CMS membrane is to further enhance both the permeability and separation performance. One of the subjects of the present study was therefore to investigate whether it is possible to increase the permeability by forming nanospaces that can be used for gas molecules to permeate through. Here we report effects of alkali metal doping on the permeation performance of CMS membranes.

EXPERIMENTAL

Original CMS membranes (0.5 g), prepared by pyrolysis of Kapton-type polyimide film (125 μm in thickness) at 873-1273 K for 2 hours under vacuum, were used as host carbon. For intercalation, the membranes were added under inert gas atmosphere to an ether-type solution containing 0.2 mol/l phenanthrene and a large excess of alkali metal and agitated at room temperature for several days. Methyltetrahydrofuran (MeTHF), dimethyltetrahydrofuran (diMeTHF), Methylbutylether (MB), tetrahydrofuran (THF) and dimethylether (DME) were used as ether-type solvents. After cleaning with solvent the samples were filtered, immersed in liquid paraffin and covered with a polyethylene film to avoid de-intercalation process. Their structures were analyzed by XRD, XPS, SEM and AFM measurements. The gas permeation properties were evaluated by high vacuum time-lag method conducted at 308-373 K under the pressure difference of 1 atm. Permeabilities (in unit of Barrer, 1 Barrer = 1×10^{-10} {cm^3(STP) cm} / {cm^2 sec cmHg}) were calculated from the rate of pressure increase on the permeate side. Apparent diffusivities and sorptivities were calculated by application of sorption-diffusion model[2]. The micropore analysis was carried out by application of Dubinin-Astakhov equation[3] to the sorption isotherms of carbon dioxide at several temperatures.

RESULTS AND DISCUSSION

Characterization of Membranes

Forming a phenanthrene radical-anion complex with potassium, in which the potassium ions are coordinated with ether molecules, the intercalation process into the carbon host took place by a gradual charge transfer from phenanthrene anions to the hexagonal carbon layer. Depending on the type of ether solvents, a strong influence on the mechanical stability of the modified membranes was observed. By using MeTHF, diMeTHF and MB, which are well known to form binary potassium-GICs[4], the mechanical stability of the potassium intercalated CMS membranes was much higher, in general, than by using THF or DME, which can produce ternary potassium- GICs. The reason therefore is, that co- intercalation of organic solvents expanded interlayer spacing of graphitic region and gave mechanical stress, sometimes enough to break the membrane. Using lithium and sodium as alkali metal also lost the mechanical stability. Therefore we concentrated our following study on potassium- MeTHF- phenanthrene system (hereafter CMS- K membranes). For structure analysis XRD measurements were carried out. Unfortunately, beside the broad (002) and (004) peaks of the original CMS no further peaks were detected for the potassium- doped membranes. For graphite used as reference host carbon in the present study a third stage GIC structure was determined in accordance with the literature[5]. In contrast to the pure graphite structure the original CMS exhibits a complex turbostratic structure, in which graphite- like microcrystallines of about 8 Å in stacking size are dispersed in amorphous carbon matrix[6]. This leads to the suggestion, that the stacking of the carbon hexagonal layers is too small and/or so much disordered that all 00l diffraction lines of intercalated carbons were broadened in great detail as not to be detected, their intensities are too low, respectively. But the existence of potassium was proved by XPS analysis, which still remained even after long time Argon- etching. From these results a random stage structure is proposed for the CMS- K membranes. The general tendency for the effects of host carbon structure on the intercalation behavior agreed quite well with the literature[5].

Permeation Properties of Membranes

The permeation properties of the CMS- K membranes were characterized by using He and N_2 as analysis gases. The results presented in Figure 1 indicate that the modified membrane CMS- K1 exhibits a higher permeation as compared to that of the original one. This implies that due to the intercalation the stacked carbon hexagonal layers were expanded and/or new pathways were created, so that the gas molecules could easier diffuse through resulting in a higher permeability.

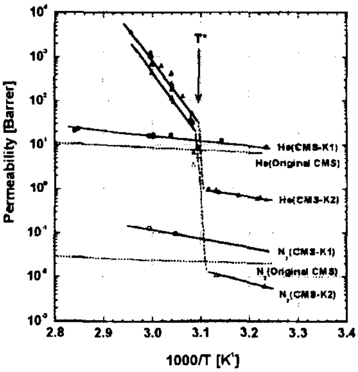

FIGURE 1 Arrhenius plots of He and N_2 permeabilities on the modified CMS membranes, CMS- K1 and K2 and on the original CMS membrane (dotted line).

It was essential to minimize the degree of de- intercalation during handling to achieve such enhanced permeation. Otherwise some hydrolysis products would be formed as a permeation barrier in between diffusion path or pore wall as well as on the membrane surface that leads to lower permeation. One good example for this is CMS- K2 membrane (Fig. 1), which additionally showed an unexpected perm- switch behavior. Normally, the gas permeability increases with increasing the temperature as shown in the case of CMS- K1 and the original CMS membranes. But the CMS- K2 membrane exhibited a permeation jump: at low temperatures the He permeabilities were about one order of magnitude lower than those of the original one. But at around T* = 323 K it raised up strongly getting three orders of magnitudes higher than the corresponding values at 308 K. This drastic change in the gas permeability in response to the temperature change was observed for this membrane with good reproducibility. The ideal separation factor for He/N_2 gas pair was about 75 at temperatures below T*. At higher temperatures there were almost no differences in the He and N_2 permeabilities any more, which implies that the membranes lost its molecular sieve ability above T*. In addition, the changes in the diffusivity and sorptivity at around T* (Fig. 2) display that the diffusivity values for CMS- K2 were lower than those of the original one, whereas the values of sorptivity were slightly higher. In contrast to this, the situation changed above T*, where the slope of diffusivity values was much higher than those of the original one. This leads to the assumption that the drastic increase in the permeability at T* is attributed to the abrupt increase in both the diffusivity and sorptivity, while the further increase in the permeability is related to the temperature- sensitive diffusion process. The reduction in permeability below T*, compared to that of the original CMS, can be explained with pore blocking effect caused by partial de- intercalation: the formation of hydrolysis products on the surface as well as within the membrane was implied by XPS, AFM and SEM analyses.

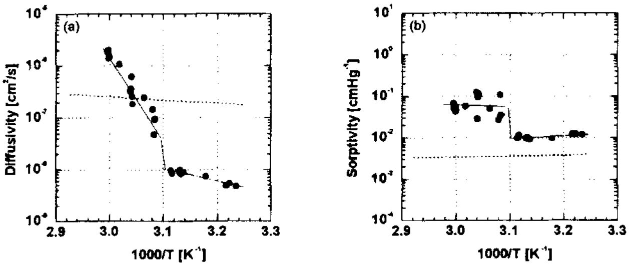

FIGURE 2 Arrhenius plots for (a) diffusivity and (b) sorptivity of helium on the CMS- K2 membrane (solid line) and on the original CMS membrane (dotted line).

The results also suggest that above T* a permeation pathway exists, large enough that larger gas molecules can easily pass through. This is supported by micropore analysis (Fig. 3) which demonstrates that above T* the micropore volume of CMS- K2 is strongly enhanced up to 0.5 cm^2/g at 333 K, while the volume of 0.2 cm^2/g remained constant for the original CMS.

The exact mechanism that causes this perm- switch behavior is not clear at present. However, structural changes like reorganization in the stage structure or rearrangement of the residue substance in crystalline and amorphous region as well as an influence of the hydrolysis layer can be possible reasons. To answer the questions, what kind of species and how they block and open the permeation pathway responding to the temperature variation, further investigations are still in progress now. Nevertheless, this perm- switch CMS is quite interesting, because it excels the existing membranes in the perm- switch and barrier properties and has potential for application in the field of sensitive supply control of reaction gases for example. To conclude, the results of the present study display the prospects to change the permeation properties of CMS membranes by alkali metal doping.

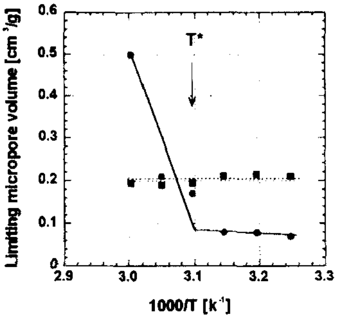

FIGURE 3 Arrhenius plots of limiting micropore volume of CMS- K2 membrane. The corresponding values for the original CMS membrane are also plotted by a dotted line.

Acknowledgments

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