탄소/실리카막의 제조 및 기체분리특성

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Preparation of Carbon/Silica Membranes and Their Gas Separation Properties

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1. Introduction

In recent years, it has been demonstrated that the diffusion controlling mechanism in carbon molecular sieve (CMS) membranes has shown an upswing of permselectivity on various gas pairs with different kinetic diameters. These CMS membranes can be usually prepared by pyrolysis of synthetic and natural polymeric precursors.

In 1983, Koresh and Soffer (1) reported the first pioneering studies for CMS hollow fibers of cellulosic or phenolic resins. Jones and Koros obtained CMS membranes from the pyrolysis of several different hollow-fiber polymeric materials, including cellulose acetate, polyaramides and polyimides (2). They reported that aromatic polyimides, considering separation and mechanical properties, were the best CMS precursors. More recently, Foley et al. reported nanoporous carbon membrane (NPC) (3,4). This NPC membranes were prepared by ultrasonic deposition of polyfurfuryl alcohol on stainless steel support and its carbonization at between 423K and 873K. The O_2/N_2 selectivity of NPC membrane carbonized at 723K was 30.4 at a permeability coefficient of 3.54 Barrer. Most of referential results were carried out by coating of the polymeric precursor on porous support in order to avoid suffering from extreme fragility. These composite materials provided high selectivities but the reproducibility was problematic (3,4). However, homogeneous flat membranes (5,6) are preferable to

investigate fundamental phenomena determining the gas permeation properties. Suda and Haraya (6) have investigated carbon molecular sieve dense membranes prepared by pyrolysis of commercially available Kapton film. The highest O_2/N_2 selectivity was 36 at a permeability coefficient of 0.15 Barrer and they showed the excellent permselectivity of the CMS membranes was primarily due to the dependence of diffusivity of penetrant on the size of the micropore.

This paper reports the synthesis and permeation properties of pyrolitic carbon/silica membrane derived from poly(imidesiloxane) (PIS) as the precursor. The imide-siloxane block copolymers was synthesized in a wide range of different siloxane content, and finally pyrolyzed at between under and Ar atmosphere. The thermal decomposition in PIS during the pyrolysis was studied by using TG-MS apparatus. The permeability and selectivity of membranes pyrolyzed at different temperatures are discussed below.

2. Experimental

2.1. Preparation of carbon/silica membranes

To investigate the effect siloxane contents on gas permeation behavior, we have synthesized polyimidesiloxanes with various siloxane contents. As mentioned above, homogeneous flat membranes are preferable to investigate fundamental phenomena to explain the gas permeation behaviors. The carbon/silica membranes were produced from the pyrolysis of poly(imidesiloxane) films with different siloxane content to investigate the effect of siloxane content on the gas permeation behavior. To optimize the pyrolysis conditions, each precursor specimen with different siloxane content was investigated by thermogravimetry (TA instrument, TGA2050)-Mass spectroscopy (Balzers instrument, Thermostar) (TG-MS). The temperature-time protocol used in this research was based on our TG-MS study. The heating temperature, one of the most important pyrolysis factors, was varied between 873K and 1273K under Ar flow. Each precursor specimen with 2.5cm×2.5cm area is pyrolyzed between two alumina plates to maintain its original shape. The carbonized membrane was then gradually cooled down to room temperature.

2.2. Characterization of carbon/silica membranes

Pyrolysis conditions such as the temperature and the heating rate are the most important factors that determine the gas separation properties and microstructure of carbon molecular sieve membrane. To optimize the pyrolysis conditions, each precursor specimen with different siloxane content was investigated by Thermogravimetry (TA instrument, TGA2050)-Mass spectroscopy (Balzers instrument, Thermostar) (TG-MS). The microstructure of the prepared carbon/silica membranes was investigated by FT IR-ATR, elemental analysis, X-ray diffractometry, scanning electron microscopy, and transmission electron microscopy and atomic force microscopy.

2.3. Gas permeation measurement

Gas permeability for various gases including ultra-high purity grade helium (0.26nm), carbon dioxide (0.33nm), oxygen (0.346nm) and nitrogen(0.364nm) were measured by constant volume method at room temperature by using a high vacuum time-lag method.

3. Results and discussion

3.1. Pyrolysis process

The carbonization of the polyimide-siloxane proceeds in two steps such as that of PMDA-ODA. The first step in the rather narrow temperature range 550-650°C, showing an abrupt weight decrease due to the evolution of a large amount of CO and CO_2. And the first step of decomposition is due mainly to a breakage at an aliphatic chains between sioxane part and imide part. The second step with small weight loss, evolution of small amounts of N_2 and H_2. From results of previous TG curves, when compared with PMDA-ODA, the initial thermal degradation of polyimide containing siloxane moiety proceeds more quickly than that of PMDA-ODA. However, the residual weight of PIS films at high temperature remained much more than that of PMDA-ODA.

3.2. Gas permeation properties

Gas separation properties of the carbon/silica membranes are plotted

in Figure 1 with respect to the so-called upper bound curve and all results lie within a commercially attractive region. Permeability had a tendency to increase with the volume fraction of siloxane in polyimide matrix without significant loss of selectivity. Poly(imidesiloxane), a polymeric precursor as carbon/silica membrane was prepared by inert purge-pyrolysis method, and this polymeric precursor might be a candidate polymer that belongs to the category of CMS membrane.

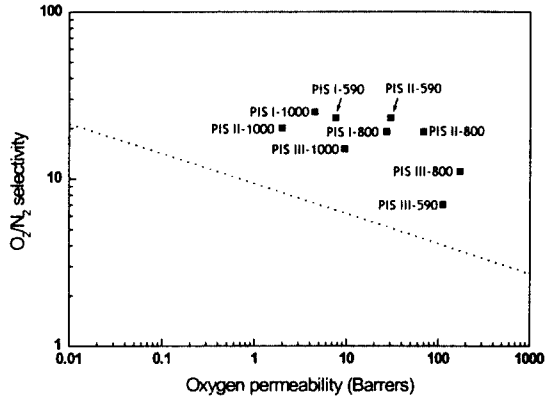

Figure 1. Oxygen permeability vs. oxygen/nitrogen selectivity of carbon molecule sieve membranes

4. References

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