

규소함유 고분자전구체로부터 제조된 탄소분자체막의 기체분리특성

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Gas Permeation Properties of Carbon Molecular Sieve Membrane Derived from Polymer Precursor Containing Silicon

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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 O₂/N₂ 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 O₂/N₂ 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 silicon-carbon molecular sieve (SCMS) membrane derived from polyimidesiloxane (PIS). The imide-siloxane block copolymer as a SCMS precursor 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 SCMS 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 SCMS membranes were produced from the pyrolysis of polyimidesiloxane 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 SCMS 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 SCMS membranes was investigated by FT IR-ATR, elemental analysis, X-ray diffractometry, scanning electron microscopy, and transmission electron 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 Kapton. 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 CO₂. And the first step of decomposition is due mainly to a breakage at carbonyl groups in the imide part. The second step with small weight loss, evolution of small amounts of H₂. From results of previous TG curves, when compared with Kapton, the initial thermal degradation of polyimide containing siloxane moiety proceeds more quickly than that of Kapton. However, the residual weight of SPI films at high temperature remained much more than that of Kapton.

3.2. Gas permeation properties

