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Preparation of 3A Zeolite-Loaded Membrane for Hydrogen Recovery from Waste Gas

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Abstract: In this study, carboxymethyl cellulose based mixed matrix membranes were prepared to remove H_2/CH_4 and CO/CH_4 gas mixtures and characterization experiments were performed. Zeolite 3A was selected as the inorganic material. It is essential in gas separation process that the membrane should be non-porous, therefore, the structure of the membrane was determined by means of polarized light microscope and contact angle test. The thermal behavior of membrane under high temperature condition was determined by using thermogravimetric analysis (TGA).

Keywords: Gas separation; mixed matrix membrane; carboxymethyl cellulose.

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INTRODUCTION

Today, the recycling of valuable gases from the waste stream is a very important issue for the chemical industry in terms of both economic and environmental aspects. Particularly, the recovery of hydrogen from the petrochemical waste stream has become the significant treatment step in the petrochemical industry. Additionally, the separation of hazardous gas from flue gases contributes to decrease the greenhouse effect.

For the separation of desired gas from gas mixtures; cryogenic distillation, pressure swing adsorption and membrane gas separation methods are commercially used. Cryogenic distillation is a selective gas recovery technique. It depends on liquefying procedure of the hydrocarbons under low temperature and high pressure conditions (1). The pressure swing adsorption is a process in which the gas is adsorbed through an adsorbent at high pressure. This method is applied without need any heat treatment process (2). However, high pressure is required to obtain ultra-pure hydrogen. Membrane gas separation is an alternative technique to recover very pure hydrogen from the other hydrocarbons by using a selective membrane. Differently from the mentioned methods, membrane separation unit covers less space. It is easy to operate this process with low operating cost. Moreover, very high purity hydrogen (99%) can be separated (1, 3) effectively.

Membrane fouling, concentration polarization, and instability in the membrane performance directly affect the performance and total operating cost of the system. One of the major factors limiting the commercial expansion of the system is the structural membrane failure under the harsh operating conditions. Additionally, low gas flux and unstable membrane selectivity restrict the commercial usage of the membrane in a gas separation method. Therefore, almost the all-academic studies related to the membrane gas separation focus on suitable membrane material selection and membrane production.

The separation pathway of a gas through a non-porous membrane has been shown in Figure 1.

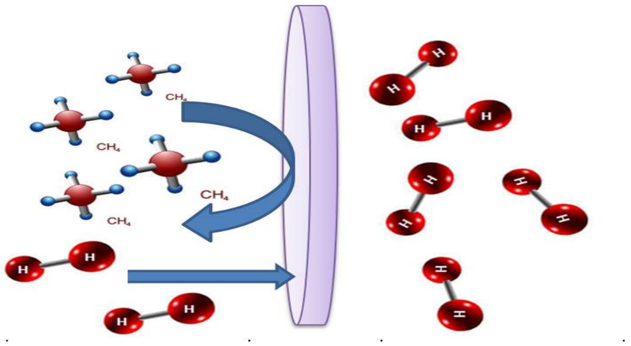

Figure 1. Molecular passage through the non-porous membrane.

In this system, selected gas molecule is removed from the gas mixture according to the molecular size of the gas and its affinity to the membrane. In the membrane gas separation system, non-porous membranes are used (4, 5). Separation behavior through the non-porous membrane is mostly explained by solution-diffusion model. This model depends on selective sorption of the gas on the membrane surface, diffusion through the membrane and desorption to the downstream side of the membrane. Membrane strength, stability, selectivity, and permeability value directly affect the performance of the system. In the membrane gas separation, driving force is the partial pressure difference between the sides of the membranes (6). Therefore, separation is maintained by the pressure difference. However, it is not the only effective parameter in this process. Besides the operating conditions such as pressure, temperature or gas composition, and structural properties of membrane material have critical importance in this system. The structural properties of the membrane are directly related to the nature of the membrane material. Inorganic, polymeric or mixed matrix dense membranes can be used as a selective membrane. Inorganic materials show resistant to severe operating conditions. However, it is difficult and expensive to manufacture inorganic membrane. Polymeric membranes are frequently used as gas separation membrane (7, 8). It is easy to form polymeric materials as a membrane with a different module. Yet, the polymeric membranes have relatively low chemical and thermal resistance. Hence, the operating lifetimes of the polymeric membranes are relatively short. Polymeric membranes can be characterized into two main classes; rubbery and glassy types according to the segmental structure of polymers. Because of the limited free volume of glassy ones, they are preferable to be used for the separation of small gas molecules from hydrocarbons (such as hydrogen removal from carbon dioxide or methane). In order to increase the stability of polymeric materials, inorganic filler incorporated polymeric membranes have been improved. Homogeneous distribution of inorganic particles in a polymeric matrix also increases the tortuous pathway and improves the selectivity of small-size gas molecules through the membrane. For these purposes, zeolites, clays, and inorganic or metallic based materials can be used (3).

The aim of this study is to manufacture a selective membrane to be used to separate hydrogen from methane and carbon dioxide. Hydrogen has a relatively small kinetic diameter than that of methane and carbon dioxide, therefore, it is important to manufacture a selective membrane that has small free volume. It is known that the glassy polymers have limited free volume spaces. Hence, carboxymethyl cellulose (CMC) has been chosen as the polymeric matrix. In order to restrict the free volume spaces and the chain mobility of the polymeric matrix, zeolite 3A has been selected as the inorganic filler. It is also expected to increase the thermal resistance of the membrane by zeolites incorporating. Additionally, a cross-linking procedure has been applied to restrict the chain mobility of the polymer.

MATERIALS AND METHODS

Materials

Carboxymethyl cellulose, 3A zeolite, and glutaraldehyde were purchased from Aldrich Chemicals, Turkey. HCl, acetone, and ethanol were supplied from Merck Chemicals, Turkey.

Method

In this study, 3A distributed CMC mixed matrix membrane was prepared by phase inversion method. For this purpose, 7 wt. % CMC-water solution was prepared and stirred at 55 °C until a homogeneous solution was obtained. Afterward, 3A zeolites (with weight ranging between 10% - 50%) were added to the polymer solution by using "priming method" which was described in the previous study (9). Priming is a procedure to prevent a non-adhesive contact between the polymer and inorganic particle. It is important to combine these two different structures for preparation a good selective membrane. A possible incompatible area between the polymer and zeolite may cause a reduction in gas selectivity values. Especially, in the case of the selective hydrogen recovery, the diameters of almost all organic chemicals are larger than the size of a hydrogen molecule. Hence, it is possible to restrict the non-selective passage of other molecules by preventing contact-free region between the polymer and zeolite.

Characterization

In this study, several characterization experiments were performed to determine the structural properties of the membrane, which would affect the membrane gas permeability. Sessile drop water contact angles of the pristine and loaded membranes were measured by using Attension KVS Instrument. Thermogravimetric analysis (TGA) of the membrane was taken by using Mettler Toledo TGA Instrument. The TGA method was identified by the changing the temperature from 25 °C to 600 °C routinely and by recording the weight loss. Zeolite distributions in the CMC were analyzed by using Nikon Eclipse Polarized Microscope.

RESULTS AND DISCUSSION

Contact Angle Measurement

In this study, a glassy carboxymethyl cellulose polymeric membrane was used to produce a hydrogen-selective membrane. Despite the CMC was a rigid polymer, it had also flexible chain mobility and large free volume. Therefore, it was predicted that CMC could give low hydrogen selectivity without a structural improvement. To improve that failure, 3A zeolite was incorporated into CMC matrix. 3A has very small cage size that only allows to hydrogen molecule passage over the methane and carbon dioxide. Additionally, 3A zeolite contributes to decelerate the diffusions of the larger ions by increasing the tortuous pathway. Contact angle measurements were shown in Figure 2.

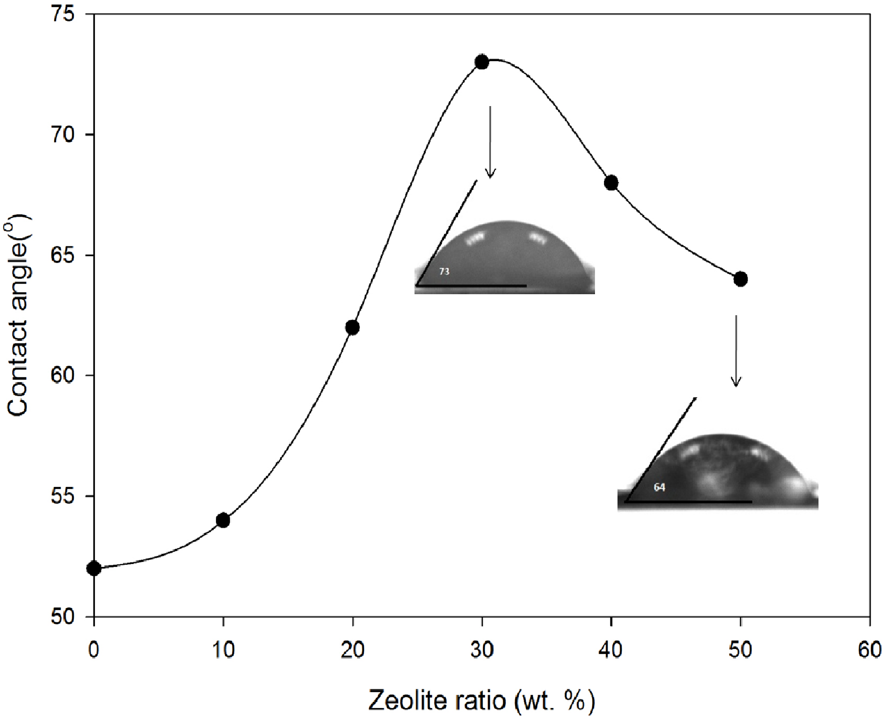

Figure 2. Contact angle measurement of mixed matrix membrane.

Addition of zeolite particles into CMC increased the water uptake capacity of the membrane. However, after a certain loading, angles decreased due to the tight and continuous zeolite phase in the membrane. With the help of the contact angle measurements, it is possible to predict that the decreasing molecular species could restrict the non-selective passage of other molecules and could increase the hydrogen selectivity.

Polarized Electron Microscope Results

In Figure 3, electron microscopy images under polarized light are shown. While the dark region represented the polymeric matrix, light phase showed the zeolite particles on the surface of the membrane.

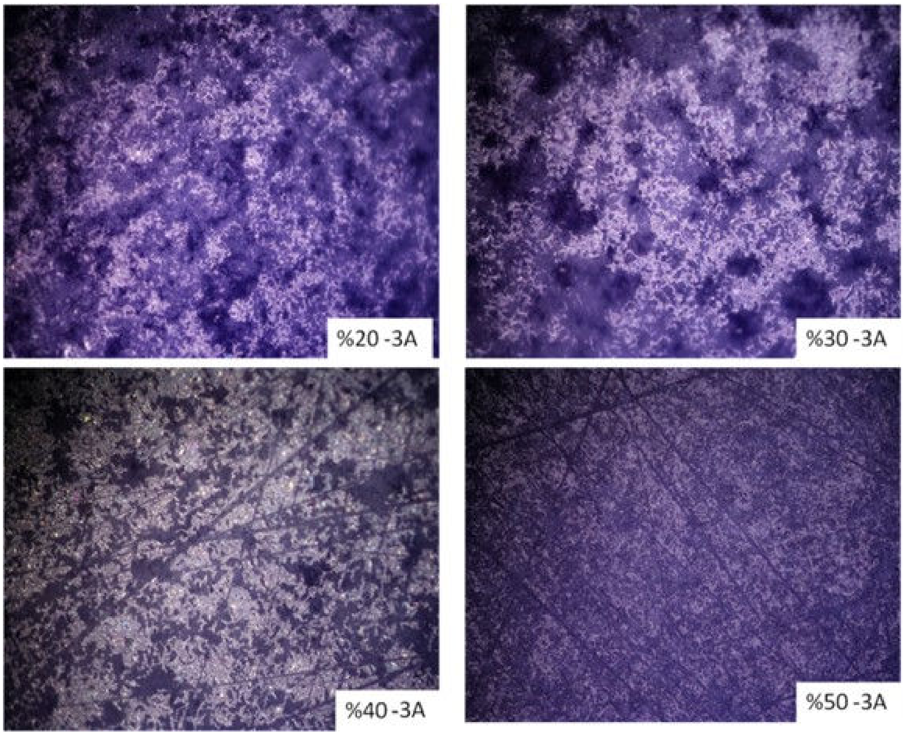

Figure 3. Zeolite distribution on polymeric matrix.

As seen in Figure 3, when the amount of zeolite increased in the membrane, the continuous phase distribution of the zeolite on the membrane surface increased. Despite this increment, there was no aggregation on the surface. A homogeneous dispersion was observed from the microscopy images. It was also found that the surface of 40 wt. % and 50 wt. % of zeolite loaded membranes were fully coated by zeolite.

Thermogravimetric Analysis

One of the biggest disadvantages of the polymeric membrane usage is the low thermal resistance of polymeric materials. It is known that the inorganic particle addition into polymeric membrane improves the thermal resistance of the membrane according to the rule of mixture (10). The industrial waste gases are generally produced followed by hot processes. Therefore, the membrane to be used in gas separation system should have high thermal resistance. Besides the high selective separation properties of the membrane, this study focused on the improving of thermal resistance of membrane by zeolite addition as well. Figure 4 shows the thermal behavior of pristine and zeolite loaded CMC membrane. As such, it can be evaluated from the figure that the thermal resistance of the membrane increased by zeolite addition.

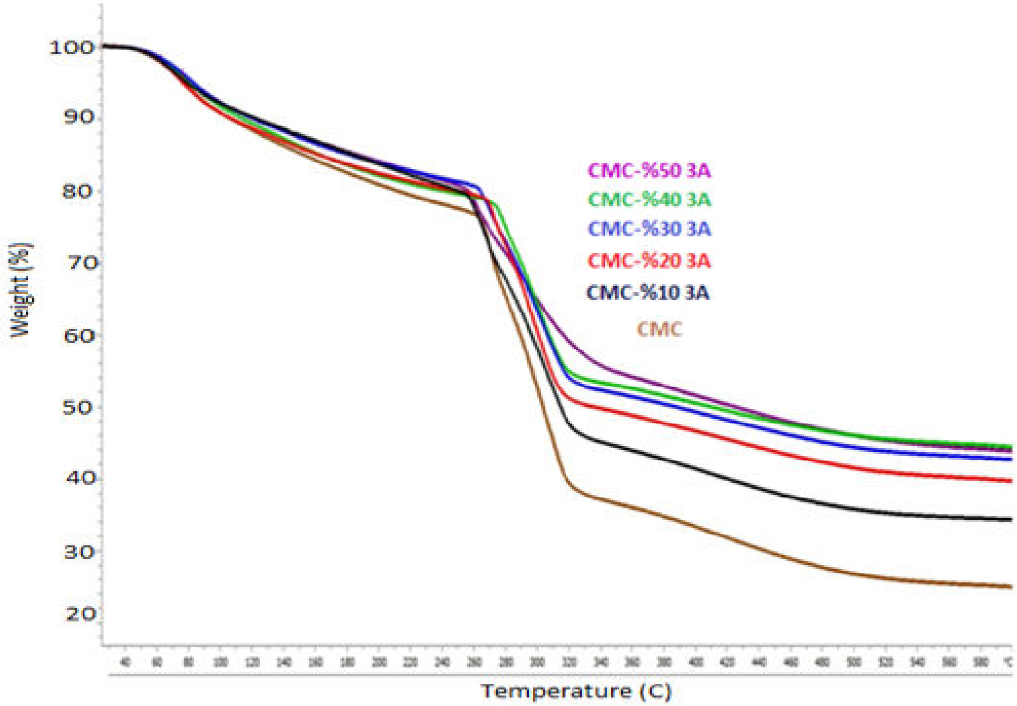

Figure 4. TGA results of pristine and zeolite loaded membrane.

CONCLUSIONS

In this study, 3A loaded carboxymethyl cellulose mixed matrix membrane was prepared to be used for hydrogen recovery from other gases such as carbon dioxide or methane and characterization tests were performed. As a result of the characterization tests, it was seen that the thermal resistance of the membrane increased by zeolite addition. It is clear from the characterization findings that the physical and chemical properties of membranes changed from polymeric to inorganic by zeolite addition. When the zeolite ratio increased, the capacity of water penetration in the membrane surface was increased and it was confirmed by contact angle measurements. In other words, the mixed matrix membrane restricted the molecular void spaces of the polymer. As a result, it is possible to consider that the prepared mixed matrix membrane is suitable for selective hydrogen recovery by membrane gas separation method.

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Türkçe öz ve Anahtar Kelimeler

Atık Gazlardan Hidrojen Gerikazanımı için 3A Zeoliti Katkılı Selüloz Membranların Hazırlanması

Filiz UĞUR NİGİZ, Nilüfer DURMAZ HİLMİOĞLU

ÖZET: Bu çalışmada, H_2/CH_4 ve CO/CH_4 ayrılmasına yönelik karboksimetil selüloz temelli karma matrisli membranlar hazırlanmış ve karakterizasyon testleri yapılmıştır. Inorganik malzeme olarak 3A zeoliti seçilmiştir. Membranın gözeneksiz olması yüksek seçicilik için önemlidir bu nedenle gözeneksiz yapı polarize ışınlı mikroskop ve temas açısı testleri ile belirlenmiştir. İnorganik malzeme eklenmesi ile membranın yüksek sıcaklığa dayanması amaçlandığı için 3A katkısının termal dayanıma etkisi termal test (TGA) ile belirlenmiştir.

Anahtar Kelimeler: Gaz ayırma; karma matrisli membran.

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