学 位 論 文 審 査 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　ジャン ヤチ

審査担当者	主査	教授	向井 紳
	副査	特任教授	荒井 正彦
	副査	教授	福岡 淳
	副査	教授	増田 隆夫

学 位 論 文 題 名

Membranes Made with Zeolite and ZIF-8, and Their Applications to Water Separation from Organic/Water Mixtures
（ゼオライト膜及び ZIF-8 膜の合成と有機物水混合溶液分離への応用）

A new separation process has been proposed to achieve highly separation with minimum energy comsuption instead of the separation processes using traditional distillation column. A pervaporation by using a membrane is a promising technique for this new process, and it is strongly desired to realize the separation process using inrganic membranes, especially under the conditions of high temperatures, where polymer menbranes cannot be applied. The main objective of this study is to prepare zeolite membranes as inorganic membranes, and to apply them to selective separation of water from water/organic mixtures by pervaporation technique in order to verify their effectiveness.
The thesis is constituted by 6 sections from chapter 1 to chapter 6.
In chapter 1, the industrial separation process using distillation columns is intriduced, and its problems are extracted. Furehtmore, the nature of zeolites is overviewed, and the expection of zeolite membranes is described for a new separation process.
In chapter 2 and 3, the research results concerning with mordenite membrane are discussed. In chapter 2, mordenite nanocrystal-layered membranes consisting of a mordenite nanocrystal layer and protection layer were successfully prepared. The effect of nanocrystal layer thickness was investigated to optimize the preparation condition of the membrane. The acid-tolelance of the prepared membrane was examined by conducting selective water separation from acetic acid/water solution. In chapter 3, the effect of the polarity of the organic solvent in the feed solution on the permeance of water through the membrane was studied. The performance of the prepared membrane is strongly affected by the preparaton conditions, such as hydrothermal temperature, pre-aging time for the mother liquid using for hydrothermal synthesis and heating rate during the hydrothermal synthesis. In order to prepare the membrane with high separation ability and permeability, the effects of these conditions on the membranes performance were discussed. Moreover, the prepared mordenite membranes were applied to the separation of water from water/organic solutions (organic solvents: ethanol, acetone, 2-propanol, or acetic acid) using a pervaporation method, and the effectiveness of the membranes were verified.
In chapter 4 and chapter 5, MTW zeolite as a new type high-silica material with a unidimensional 12-membered ring channel were used to prepare the membrane. At first, the MTW nanocrystals with different Si/Al ratios were successfully synthesized using different kinds of the organic structure directing agents (OSDA), to use them as seed crystals for membrane preparation. Using thus obtained the nanocrystals, MTW-type zeolite nanocrystal-layered membranes composed of nanocrystal and protection layers were prepared by a secondary growth method under hydrothermal conditions. The acid-tolelance properties of the membranes were observed through the pervaporation experiments for separating water from acetic acid/water solution. MTW zeolite can be synthesized in a wide range of Si/Al ratio, and

the crystals morphology of MTW zeolite can be control by using different kind of the OSDA molecules. Therefore, in chapter 5, the effects of crystal morphology, Si/Al ratio and thickness of MTW zeolite membrane were discussed on the separation performance of the membrane using water/2-propanol solution as the permeate of the pervaporation experiment. On the basis of the experimental data, the mechanism of the MTW type zeolite membrane was also discussed, and the optimal properties of the protection layer and the nanocrystal layer in the membrane were clarified.
In capter 6, zeolitic imidazolate frameworks (ZIFs) as metal-organic frameworks (MOF) were focused. ZIFs possess the advantages of both zeolites and MOFs, namely molecular sieving effect, hydrophilic and hydrophobic properties. Therefores, the nanocrystals and the membranes of ZIF-8 as a model ZIFs were prepared. In order to understand the properties of ZIF-8 materials, the gas adsorption isotherms of ZIF-8 crystals were measured in advance. The permeance performance of single component (water, ethanol, butanol, benzene, hexane) through ZIF-8 membrane was found to follow the adsorption properties obtained through the gas adsorption experiment using ZIF-8 crystals.
In conclution, the new type hydrophilic membranes have been prepared successfully, and applied to selective water separation from organic/water mixtures. Moreover, the separation mechanisms in the zeolite membranes have been clarified from their permeation performance. The results from this work are considered to be useful for developing a new membrane technology in the separation process.
Based on the reasons mentioned above, it is considered that the applicant is considered to be qualified for receiving doctoral degree of engineering from Hokkaido University.