

## 論文の内容の要旨

論文題目 Study on Hydrogen Selective Silica-based Membrane for Ethane Dehydrogenation over Cr/ZSM-5 Catalyst  
(ZSM-5 担持クロム触媒を用いたエタンの脱水素化の膜反応器に関する研究)

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Ethylene is one of the most important petrochemicals due to its extensive use as feedstock for the production of a vast array of chemicals, including polymers (e.g., polyethylene, polyvinyl chloride and polystyrene), oxygenates (e.g., ethylene oxide, ethylene glycol, and glycol ethers), and chemical intermediates (e.g., ethylbenzene and ethylene dichloride). The current worldwide production of ethylene amounts to 160 million tons per year. Ethylene is commercially produced by steam cracking and fluid catalytic cracking of naphtha, light diesel, and other oil byproducts, but these processes require high-energy and are not selective, producing substantial quantities of methane and coke as byproducts. In this respect, catalytic dehydrogenation of ethane provides an alternative for producing ethylene with hydrogen as a byproduct, an important reagent in refineries. One of the drawbacks of catalytic dehydrogenation of ethane is the thermodynamic constraints in the ethane conversion. To alleviate this problem, membrane reactors are considered possible solutions because they can overcome the equilibrium limitation of the reaction by extracting H<sub>2</sub> continuously from the catalyst bed.

Membranes with high H<sub>2</sub> permeance and selectivity could contribute to the development of new hydrogen separation technology, and have been researched extensively. Hydrogen-selective membranes include organic polymers, microporous ceramics, dense metals, and silica glasses. The silica-based materials are promising for high purity hydrogen production and separation with high chemical resistance and thermal stability, as well as moderate cost. However, the instability of silica materials, especially in the presence of steam, limits their use in applications such as high-temperature

membrane reactors. Prolonged exposure to the silica to water vapor at elevated temperatures causes rapid densification that leads to a decrease in the permeability of the membranes.

This thesis deals with the study of hydrogen selective silica-based membranes for ethane dehydrogenation over Cr/ZSM-5 catalyst. First, silica-based membranes were developed to improve their permeability and hydrothermal stability by modifying precursors. The morphology and structure of prepared membranes were discussed, and permeance mechanisms of small and large gases through the membranes were studied with experimental and simulated data. Second, the effect of various reaction conditions, including feed flow rates, pressures, and temperatures, on dehydrogenation of ethane over Cr/ZSM-5 catalyst was investigated in a conventional packed-bed reactor (PBR) and in a membrane reactor (MR) fitted with modified silica membranes. A performance of membrane reactor was evaluated using parameters including an ethylene yield enhancement and an operability level coefficient (OLC), which is the ratio between the actual permeation rate and the actual formation rate of H<sub>2</sub> in a membrane reactor.

Chapter 1 describes the general introduction of global ethylene production, hydrogen-selective membranes and ethane dehydrogenation in a membrane reactor.

Chapter 2 describes the preparation and permeation properties of zirconia modified silica membranes. The silica-zirconia composite membranes were prepared on porous alumina substrates by employing chemical vapor deposition (CVD) with varying molar ratio of tetraethylorthosilicate (TEOS) and zirconium (IV) *tert*-butoxide (ZTB) at 923 K. The resulting membrane had a high H<sub>2</sub> permeance of  $3.8 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  with selectivities over CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> of 1100, 1400 and 3700 at 923 K, respectively. Studies of the temperature dependence of the permeance of He, H<sub>2</sub>, and Ne demonstrated that the permeation mechanism was similar to that of dense silica membranes, involving solid-state diffusion with jumps of the permeating species between solubility sites. Parameters such as the site density, jump distance, and jump frequency were calculated and were physically plausible, and varied in a reasonable manner with the mass and size of He, H<sub>2</sub>, and Ne. The silica-zirconia membrane showed hydrothermal stability over a testing period of 48 h. After exposure to 16 mol% water vapor at 923 K for 48 h, a pure silica membrane showed a 68 % decline with a H<sub>2</sub> permeance  $4.5 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a H<sub>2</sub> over N<sub>2</sub> selectivity of 800, both of which continued to deteriorate. In comparison, a 10 % zirconia-silica membrane showed a decline of 56 % but to a level of  $10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  with a H<sub>2</sub> over N<sub>2</sub> selectivity of 5700. Importantly, the deterioration largely stabilized at that point.

Chapter 3 describes the synthesis and characterization of modified silica membrane prepared by CVD of vinyltriethoxysilane (VTES) at 873 K at atmospheric pressure. The membrane had a high H<sub>2</sub> permeance of  $5.4 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  with H<sub>2</sub> selectivity over CO<sub>2</sub>, N<sub>2</sub>, CO and CH<sub>4</sub> of 95, 170, 170

and 480 at 873 K, respectively. In situ Fourier transform infrared (FTIR) measurements after CVD on an alumina disk at the same conditions as for the membrane preparation showed that the vinyl groups remained in the silica structure. The VTES-derived membrane had higher hydrothermal stability than a pure TEOS-derived silica membrane, during exposure to 16 mol% water vapor at 872 K for 72 h. The temperature dependence of the permeance of various molecules (He, Ne, H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CO, CH<sub>4</sub>) before and after hydrothermal treatment gave information about the mechanism of permeance and the structure of the membrane. The membrane was composed of a contiguous silica network through which small species permeated by a solid-state mechanism and a small number of pores through which the large molecules diffused. The silica-based structure became more compact after hydrothermal treatment with decreasing permeance of small molecules (He, Ne, H<sub>2</sub>), while small pores were enlarged increasing permeance of large molecules (CO<sub>2</sub>, N<sub>2</sub>, CO, CH<sub>4</sub>). Calculation results for the small species based on a mechanism involving jumps of the permeating species between solubility sites showed lower activation energy and larger jump distances than those of a TEOS-derived silica membrane. The retention of the vinyl groups in the structure mostly associated with the defect pores resulted in interactions with CH<sub>4</sub> and CO<sub>2</sub>, so that these species permeated by a surface diffusion mechanism.

Chapter 4 describes the dehydrogenation of ethane over 5 wt% Cr/ZSM-5 catalysts in a conventional packed-bed reactor (PBR) and in a membrane reactor (MR) fitted with a hydrogen-selective silica membranes at various feed flow rates, total pressures, and temperatures. The silica membrane was prepared by the chemical vapor deposition of vinyltriethoxysilane (VTES) at 873 K, and the membrane had a high H<sub>2</sub> permeance of  $2.7 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  with H<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> selectivity of 250 and 240 at 573 K, respectively. The H<sub>2</sub> permeance at reaction conditions was similar to that obtained with single gas permeance measurement in the range of  $2\text{-}3 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . Cr/ZSM-5 catalysts were successfully synthesized, which were characterized by Brunauer-Emmett-Teller (BET), X-Ray diffraction (XRD) and X-ray absorption fine-structure (XAFS) measurements. The analyzed results show that the active phase of the catalyst was Cr<sub>2</sub>O<sub>3</sub>. The effect of various reaction conditions including feed flow rates, total pressures, and temperatures on the dehydrogenation of ethane were investigated in the PBR and the MR. At all reaction conditions, conversion of C<sub>2</sub>H<sub>6</sub> and yields of C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> in the MR were higher than those in the PBR. Importantly, the productivity in H<sub>2</sub> formation increased with increasing pressure even though the conversion of C<sub>2</sub>H<sub>6</sub> and yield of C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> decreased. The yield enhancement of C<sub>2</sub>H<sub>4</sub> and an operability level coefficient (OLC), the ratio between the actual permeation rate and the actual formation rate of a H<sub>2</sub> in a membrane reactor, obtained from the experiment and modeling simulation were used to evaluate the MR, and the C<sub>2</sub>H<sub>4</sub> yield enhancement was well correlated with the OLC

values.

Chapter 5 describes general conclusions of the thesis, including the findings of the modified silica-based membranes and ethane dehydrogenation in a membrane reactor with the prepared hydrogen selective silica-based membranes. It also presents suggestions for future work, which would lead to the improvement of the performance of membrane reactor for ethane dehydrogenation.