審査の結果の要旨

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The papers written by So-Jin Ahn for her thesis concern the subject 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_2 in a membrane reactor.

Permeation properties of silica-zirconia composite membranes supported on porous alumina substrates, So-Jin Ahn, Atsushi Takagaki, Takashi Sugawara, Ryuji Kikuchi and Shigeo Ted Oyama, Journal of Membrane Science 526 (2017) 409-416.

This paper 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_2 permeance of 3.8×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with selectivities over CO_2, N_2 and CH_4 of 1100, 1400 and 3700 at 923 K, respectively. Studies of the temperature dependence of the permeance of He, H_2, 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_2, 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_2 permeance 4.5×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and a H_2 over N_2 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} mol m^{-2} s^{-1} Pa^{-1} with a H_2 over N_2 selectivity of 5700. Importantly, the deterioration largely stabilized at that point.

Synthesis and characterization of hydrogen selective silica membrane prepared by chemical vapor deposition of vinyltriethoxysilane, So-Jin Ahn, Gwang-Nam Yun, Atsushi Takagaki, Ryuji Kikuchi and Shigeo Ted Oyama, Journal of Membrane Science 550 (2018) 1-8.

This paper deals with the synthesis and characterization of modified silica membranes prepared by CVD of vinyltriethoxysilane (VTES) at 873 K at atmospheric pressure were describes in this part. The membrane had a high H_2 permeance of 5.4×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with H_2 selectivity over CO_2, N_2, CO and CH_4 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_2, CO_2, N_2, CO, CH_4) 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_2), while small pores were enlarged increasing permeance of large molecules (CO_2, N_2, CO, CH_4). 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_4 and CO_2, so that these species permeated by a surface diffusion mechanism.

Dehydrogenation of ethane over Cr/ZSM-5 catalyst in a hydrogen selective silica membrane reactor, So-Jin Ahn, Gwang-Nam Yun, Atsushi Takagaki, Ryuji Kikuchi and Shigeo Ted Oyama, Separation and Purification Technology 194 (2018) 197-206.

This paper 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 were describes in this part. The silica membrane was prepared by the chemical vapor deposition of vinyltriethoxysilane (VTES) at 873 K, and the membrane had a high H_2 permeance of 2.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with H_2/C_2H_6 and H_2/C_2H_4 selectivity of 250 and 240 at 573 K, respectively. The H_2 permeance at reaction conditions was similar to that obtained with single gas permeance measurement in the range of $2\text{-}3 \times 10^{-7}$ mol m^{-2} s^{-1} 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_2O_3. 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_2H_6 and yields of C_2H_4 and H_2 in the MR were higher than those in the PBR. Importantly, the productivity in H_2 formation increased with increasing pressure even though the conversion of C_2H_6 and yield of C_2H_4 and H_2 decreased. The yield enhancement of C_2H_4 and an operability level coefficient (OLC), the ratio between the actual permeation rate and the actual formation rate of a H_2 in a membrane reactor, obtained from the experiment and modeling simulation were used to evaluate the MR, and the C_2H_4 yield enhancement was well correlated with the OLC values.

The collection of papers meets the requirements for the doctoral degree in engineering and can be judged to contribute to the development of chemical systems engineering.