Reaction of Methanol Using ZSM-5 Zeolite Membrane Reactor with Controlled Acid Site Distribution

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ABSTRACT

Zeolites have micro pores within their crystals, diameters of which are almost equal to molecular diameters of lighter hydrocarbons. Therefore, zeolite membranes without any pinholes are expected to show high performance for shape selective separation of hydrocarbons. Moreover, by applying the zeolite membrane with catalysis to reaction in series, there is the possibility for producing intermediate species at higher yields than in those using conventional reactors. In this study, catalytic ZSM-5 zeolite membranes were employed to a reaction of methanol to olefins (MTO reaction). The ZSM-5 zeolite catalyst membrane without pinholes was successfully prepared by synthesizing a ZSM-5 zeolite layer on an outer surface of a cylindrical alumina ceramic filter. The membrane was used as the catalytic membrane reactor to recover olefins from methanol. Though olefins were successfully produced at a high selectivity from methanol, the paraffin production was observed at the feed side of the zeolite membrane. In order to inhibit the production of paraffin and aromatics, the acid site distribution of the ZSM-5 zeolite membrane was controlled by CCS method (Catalytic Cracking of Silane method developed in our laboratory). Deactivation of acid sites at the outer surface of the zeolite membrane (feed side of reactant) by the CCS method enable to increase the selectivity of olefins and decrease in the selectivities of paraffin and aromatics.

KEYWORDS
Zeolite, ZSM-5, catalytic membrane, catalytic cracking of silane, methanol to olefin

INTRODUCTION

Zeolites, crystalline alumino-silicates, have been widely used in industry as heterogeneous catalysts and adsorbents, because of their high activity and high capacity for adsorption. Moreover, zeolites crystals have micropores with diameters almost equal to those of lighter hydrocarbons. Therefore, zeolite membranes without any pinholes would be expected to show high performance for the shape-selective reaction and separation of hydrocarbons. There have been many research works on the synthesis and applications of the zeolite membranes, such as high siliceous MFI-type zeolite (Silicalite-1) (Kusakabe, et al., 1996), A-type zeolite (Masuda, et al., 1995), mordenite (Matsukata, et al., 1994) and faujasite (Hasegawa, et al., 2001) membranes. We have also succeeded in preparing a MFI-type zeolite (ZSM-5 and silicalite-1) membranes without any pinholes (Masuda, et al., 2003). Moreover, these membranes exhibited molecular sieving effects for xylene and diethylbenzene isomers, and catalytic activity for methanol to olefin synthesis with high selectivity above 80 %. However, paraffin and aromatic compounds were also produced at the feed side of the membrane due to non-shape selective reactions over acid sites of the membrane faced to the feed side. In order to inhibit this over-reaction without any reductions in activity for producing olefins, the acid sites of the zeolite membrane at the outer surface (feed side) are required to be selectively deactivated. On the other hand, we have developed a method for modification of pore diameter and deactivation of acid sites of zeolite using silane compounds (Masuda, et al., 2001) (catalytic cracking of silane, denoted as CCS method). Accordingly, in this study, the CCS method was applied to selective de-activation for the
acid sites on the outer surface of zeolite membrane. Main objectives of this study were to develop a selective de-activation method for the acid sites of zeolite and to increase in the olefin selectivity.

EXPERIMENTAL

Preparation of HZSM-5 type zeolite membrane

An H-ZSM-5 zeolite membrane was hydrothermally synthesized on the outer surface of a cylindrical alumina filter (NGK Co. Ltd; 50 mm in length and 11 mm in diameter) at 473 K for 48 h, followed by calcination in an air stream. Three aqueous kinds of solutions of Na2SiO3, Al2(SO4) and NaCl were used as reactants and n-TPABr was used as a template. Sodium ions in Na-ZSM-5 zeolite membrane thus obtained was exchanged to NH4+ by a conventional ion-exchange technique using an aqueous solution of NH4NO3, washed with distilled water and heated to 773 K to yield the H-MFI type zeolite membrane with a SiO2/Al2O3 molar ratio of 50. An H-ZSM-5 zeolite catalyst powders were also prepared by the same method without the alumina support to be used for determining the optimal condition for the CCS treatment.

Control of acid site distribution of zeolite by CCS method

The H-ZSM-5 zeolite was exposed to a silane compound vapor at 373 K in a nitrogen stream, and then the feed of silane compound was stopped to remove the physically adsorbed silane compounds on the zeolite surface. The sample was heated up to 873 K to decompose silane molecules on acid sites and to leave silicon-containing carbonaceous materials on acid sites. Then the sample was calcined in air stream at 873 K, leaving SiO2 unit on each acid site. Acid site with SiO2 unit is inactive. In this CCS method, two kinds of silane compounds were employed; di-ethoxy-methyl silane (denoted as DEMS hereafter) and tri-phenyl silane (TPS). The order of molecular sizes of silane compounds and the pore size of ZSM-5 zeolite is as follows; TPS > pore diameter > DEMS. Acidic properties of the MFI-type zeolite prior to and after CCS treatment were analyzed by NH3-TPD method, which was measured under the complete adsorption equilibrium conditions (ac-TPD method) (Masuda, et al., 1997). Adsorption isotherms of benzene were obtained at 303 K by use of auto-adsorption apparatus (Bell Japan Inc, BELSORP 18 plus).

Reaction of methanol to olefin (MTO reaction)

Figure 1 shows a schematic view of a reactor made of stainless steel used for the reaction of methanol to
olefins (Kyoto Takaoshin Ltd.). One end of the membrane was sealed by alumina cement, and the remaining end was set on a sample holder using the alumina cement. Methanol was vaporized in an evaporator, and was fed to the outside of the membrane (feed side) with N₂ as the carrier gas. The reaction was continued for 2 h under the condition of a methanol feed rate of 0.6 mol h⁻¹ and a reaction temperature of 673 K. The outlet gas from the feed and the permeate sides of the membrane were separately collected by gas packs. The compositions of the products obtained from these outlets were analyzed using a gas chromatography (Shimadzu Co. Ltd., GC-14A) with porapak-Q column.

RESULTS AND DISCUSSION

Acidic properties and benzene adsorption Isotherms of ZSM-5 zeolite prior to and after CCS treatment

In the CCS method, at first, silane compounds are chemisorbed on acid sites of zeolites, followed by their decomposition in nitrogen and by calcination in air, leaving SiO₂ units. Therefore, the location of acid sites covered by silane compound coincides with that of acid sites covered by SiO₂ units. Accordingly, in order to investigate the effects of the molecular size of silane compounds on the changes in amounts of acid sites and in pore structure of the ZSM-5 zeolite, NH₃-TPD spectra and benzene adsorption isotherm of the ZSM-5 zeolite were measured prior to and after CCS treatment. In the preliminary experiments, it was revealed that all zeolite samples treated by the CCS method were inactive in the trans-alkylation’s reaction of 1,3,5-tri-methyl-benzene, indicating that the acid sites of zeolite on the outer surface were deactivated because of the formation of SiO₂ units by the CCS treatment.

Figure 2 shows ac-NH₃-TPD spectra of the zeolite samples prior to and after the CCS treatment using DEMS and TPS. The amount of acid sites of the zeolites after the CCS treatment decreased as compared with the fresh sample. As mentioned above, since the SiO₂ units were formed on the outside of the zeolite at the outer surface of its crystal by the CCS treatment, the decrease in the amount of acid sites was the predicted results. However, the decrease in the amount of acid sites depended on the type of silane compounds, and the sample treated by DEMS exhibited the marked decrease in the amount of acid sites as compared with the sample treated by TPS.

Figure 3 shows the benzene adsorption isotherms of the zeolite samples prior to and after the CCS treatment. The molecular size of benzene is approximately equal to the pore diameter of a fresh ZSM-5 zeolite. Accordingly, when SiO₂ is formed by CCS method on the acid sites on the zeolite pore, benzene molecules encounter the difficulty in penetrating into the pores. As shown in Fig 3, the amount of benzene adsorbed within the zeolite after the CCS treatment using DEMS was extremely decreased, indicating that the SiO₂ units were formed on the acid sites inside pores of the zeolite crystals as well as the outer surface. On the contrary, the benzene adsorption

![Figure 2. Change in the NH₃-TPD profiles of caused by SiO₂ formation of acid sites of ZSM-5 zeolite.](image)

![Figure 3. Adsorption isotherms of benzene on ZSM-5 zeolites prior to and after CCS treatment.](image)
isotherm of the zeolite prior to and after the CCS treatment using TPS was almost the same.

While NH$_3$ molecules can pass through parts in pores where SiO$_2$ unit is formed, benzene cannot diffuse through the parts. Accordingly, the decrease in the amount of acid sites shown in Fig. 2 represents the number of acid sites covered by SiO$_2$ units, and the decrease in the amount of adsorbed benzene shown Fig. 3 corresponds the pore space where is completely blocked by SiO$_2$ units for benzene molecules. Therefore, these results indicated that the selective adsorption of TPS occurred on acid sites on the outer surface of zeolite crystals due to its large molecular size. On the other hand, for the case of DEMS, the acid sites both inside and on the outer surface of zeolite crystals were covered by SiO$_2$ units. The results described above indicate that the distribution of acid sites of ZSM-5 zeolite can be controlled by the CCS method with silane compounds of different minimum molecular sizes.

**Conversion of methanol to olefins using ZSM-5 catalytic membrane**

In order to prevent reactions of methanol to paraffin and aromatics in the feed side of the membrane, it was considered that the acid sites at the outer surface of the ZSM-5 zeolite catalytic membrane should be selectively deactivated by the CCS method employing TPS. Figure 4 shows the typical production selectivity using the ZSM-5 catalytic membranes prior to and after the CCS treatment using TPS. The experimental conditions were reaction temperature of 673 K, methanol feed rate ($F$) of 0.6 mol h$^{-1}$ and an index of time factor ($A/F$) of 1.7×10$^{-3}$ m$^{2}$ mol$^{-1}$ h. Though olefins were obtained at the permeate side, the production selectivity of paraffin at the feed side was much higher than that of olefins at permeate side. The paraffin production at the feed side resulted from the reaction of methanol to paraffin for acid sites at the outer surface of the zeolite catalytic membrane. Moreover, chain length of the paraffin at the feed side was longer than that of olefins and paraffin observed at the permeate side.

On the contrary, the production selectivity of paraffin was markedly decreased at the feed and the permeate sides using the zeolite membrane treated by CCS method. Moreover, the olefin production at permeate side was higher than that at the feed side. These results indicated that the reaction in series of methanol at the feed side of the zeolite membrane was inhibited. In other word, since the acid sites on the zeolite membrane at the outer surface were deactivated by the CCS method using TPS, the paraffin production from methanol was inhibited at the feed side. Accordingly, the methanol which diffused into the zeolite membrane was converted into olefin, the production selectivity of which was increased at the permeate side.

**Dependency of olefin yield on methanol conversion**

Figure 5 shows the relationship between the methanol conversion and the molar fraction of olefins in products.
recovered from the permeate side of the membrane. The data from a fixed bed type reactor and the catalytic zeolite membrane prior to the CCS treatment were also plotted for comparison. Compared with the fixed bed type reactor, the catalytic zeolite membrane exhibited the high selectivity of olefins at the high conversion of methanol. Moreover, by applying the CCS method to the catalytic zeolite membrane, the selectivity of olefins was improved. This resulted from the selective deactivation of the acid sites at the outer surface of the catalytic zeolite membrane, which could inhibit the production of paraffin and aromatics.

CONCLUSIONS

A ZSM-5 zeolite membrane without any pinholes was successfully prepared on the outer surface of a cylindrical alumina ceramic filter. The membrane exhibited the catalytic activity for the reaction of methanol and high selectivity of olefins, which is the intermediate species in the reaction. However, undesirable reaction of methanol to paraffin and aromatics proceeded at the outer surface of the membrane (feed side). In order to inhibit the production of paraffin and aromatics, the acid site distribution of the ZSM-5 zeolite membrane was controlled by CCS method using silane compounds with different molecular diameters (di-ethoxy-methyl silane; DEMS and tri-phenyl silane; TPS). By using TPS as a SiO2 unit-forming agent, the acid sites at the outer surface of ZSM-5 zeolite crystals could be selectively deactivated. The selective deactivation of acid sites distributed on the outer surface of the zeolite membrane (feed side of reactant for the reaction of methanol) by the CCS method led to a decrease in the production of paraffin and aromatics at the feed side. The olefins selectivity reached 85 % at the methanol conversion of 40%.

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REFERENCES


