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Control of acid-site location of ZSM-5 zeolite membrane and its application to the MTO reaction

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Abstract

ZSM-5 zeolite membrane, which shows high selectivity toward olefins in the methanol conversion, was developed by controlling the location of the acid sites. First, 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 the olefins were successfully produced from methanol with high selectivity (ca. 80%), production of paraffin and aromatics was observed at the feed side of the zeolite membrane. To prevent the such production, the location of the acid site of the ZSM-5 zeolite membrane was controlled by a new method called the catalytic cracking of silane (CCS) method. Selective deactivation of acid sites at the outer surface of the zeolite membrane (feed side of reactant) by the CCS method allowed us to increase the selectivity of the olefins by 10% as compared to the untreated membrane.

Keywords: ZSM-5 zeolite; Catalytic membrane reactor; Catalytic cracking of silane; Methanol to olefin; Acid site

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1. Introduction

Zeolites, crystalline alumino-silicates, have been widely used in industry as heterogeneous catalysts because of their high activity and high capacity to adsorb to hydrocarbons. Moreover, since each kind of zeolite has micropores of a specific diameter almost equal to the diameters of lighter hydrocarbons, zeolites exhibit a remarkable molecular sieving effect for these hydrocarbons. Accordingly, 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 zeolite membranes [1] such as high siliceous MFI-type zeolite (Silicalite-1) [2–4], A-type zeolite [5,6], mordenite [7] and faujasite [8] membranes. We have also succeeded in preparing a MFI-type zeolite (ZSM-5 and silicalite-1) membranes without any pinholes [9,10]. These MFI-type zeolite membranes show molecular sieving effects for para-isomers of xylene and diethylbenzene. Moreover, the ZSM-5 membrane exhibits catalytic activity for methanol-to-olefin synthesis (MTO reaction) with high selectivity above 80%. However, paraffin and aromatic compounds are also produced in the feed side of the membrane due to non-shape-selective reactions over acid sites of the membrane facing the feed side. To prevent these non-shape-selective reactions without any reductions in olefin-producing activity, the acid sites of the zeolite membrane on the feed side must be selectively deactivated.

We have developed a method for the modification of pore diameter and deactivation of the acid sites of zeolite using silane compounds [10] (catalytic cracking of silane, denoted as the CCS method). In our previous paper, it was revealed that SiO_2 units could be formed on the acid sites of the zeolite by the CCS method, and that the ZSM-5 membrane treated by the CCS method showed the high separation factor of H_2/N_2 as compared with the membrane prior to the CCS treatment. In this study, the CCS method was also employed for selective deactivation of the acid sites on the

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outer surface of the zeolite membrane without any deactivation of acid sites in the zeolite pores. The primary objectives of this study were to develop a selective deactivation method for the acid sites of zeolite and to increase the olefin selectivity in the MTO reaction.

2. Experimental

2.1. Preparation of the H-ZSM-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 by the method in our previous paper [9]. Three kinds of water solutions were used as reactants: a sodium chloride solution, a sodium silicate solution, and an aluminum sulfate solution, and tetrapropyl ammonium bromide was used as a template. The zeolite membrane thus prepared was washed with distilled water and then dried in an air atmosphere, followed by calcination at 773 K to remove the template. Sodium ions in Na-ZSM-5 zeolite membrane thus obtained were exchanged to NH^{4+} by a conventional ion-exchange technique using an aqueous solution of 10 wt.% NH_4NO_3. The membrane was washed with distilled water, dried in air, and heated to 773 K to yield the H-MFI type zeolite membrane with a SiO_2/Al_2O_3 molar ratio of 50. H-ZSM-5 zeolite catalyst powders were also prepared by the same method without the alumina filter to be used for determining the optimal condition for the CCS treatment.

2.2. 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 the feed of silane compound was then stopped to remove the physically adsorbed silane compounds on the zeolite surface. The sample was heated to 873 K to decompose the silane compound molecules chemically adsorbed on the acid sites and to leave silicon-containing carbonaceous materials on the acid sites. The sample was then calcined in an air stream at 873 K, leaving a SiO_2 unit on each acid site, resulting in deactivation of the acid sites. In other words, the SiO_2 units were formed on the acid sites where the silane compounds were chemically adsorbed. In this CCS method, two kinds of silane compounds were employed; di-ethoxy-methyl silane (denoted as DEMS here after) and tri-phenyl silane (TPS). The order of the molecular sizes of silane compounds and the pore size of the ZSM-5 zeolite is as follows: TPS $>$ pore diameter $>$ DEMS. The acidic properties of the ZSM-5 zeolite prior to and after CCS treatment were analyzed by the NH_3-TPD method, which was carried out under complete adsorption equilibrium conditions (*ac*-TPD method) [11]. Adsorption isotherms of benzene were obtained at 303 K by use of an auto-adsorption apparatus (Bell Japan Inc, BELSORP 18 plus).

2.3. Methanol-to-olefin reaction (MTO reaction)

Fig. 1 provides a schematic view of a reactor made of stainless steel used for the methanol-to-olefin reaction. One end of the membrane was sealed by alumina cement, and the other end was set on a sample holder using the alumina cement. Methanol was vaporized in an evaporator and fed to the outside of the membrane (*feed side*) with N_2 as a carrier gas. Another N_2 line was set up to avoid stagnation of the methanol vapor in the reactor. N_2 gas was also fed to the inside of the membrane (*permeate side*) to sweep out molecules permeating from the feed side to the permeate side of the membrane. The reaction was conducted for 2 h under the following conditions: a reaction temperature of 673 K, a methanol feed rate (F) of 0.60 mol h^{-1}, and an index of time factor (A/F) of 1.7×10^{-3} m^2 mol^{-1} h, when A refers to the surface area of the membrane facing the feed side. The outlet gas from the feed and the permeate sides of the membrane were separately collected by gas packs. The

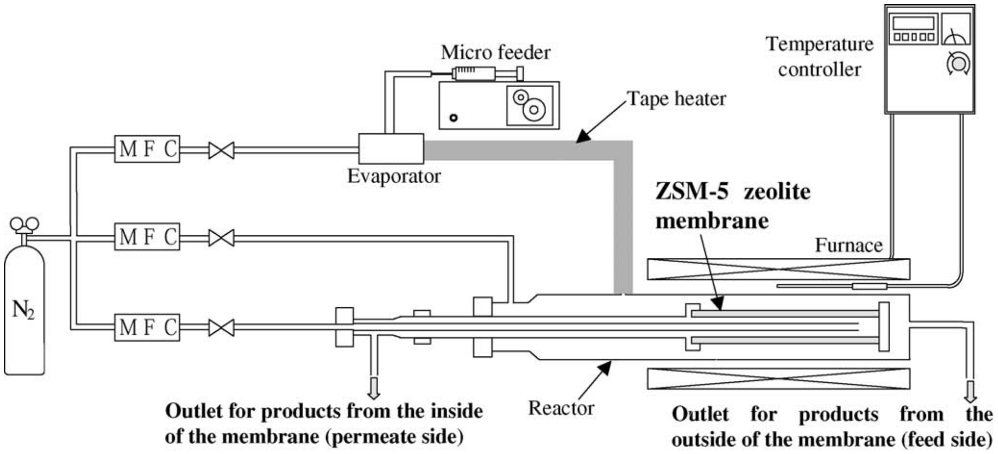

Fig. 1. Schematic view of the ZSM-5 zeolite membrane reactor.

compositions of the products obtained from these outlets were analyzed using gas chromatography (Shimadzu Co. Ltd., GC-14A) with a porapak-Q column.

3. Results and discussion

3.1. Acidic properties and benzene adsorption isotherms of ZSM-5 zeolite prior to and after CCS treatment

In the CCS method, the location of acid sites chemisorbed by silane compounds coincides with that of acid sites deactivated by SiO_2 units. To examine the possibility of controlling the location of acid sites of the ZSM-5 zeolite by the CCS method, the effects of the relative molecular size of the silane compounds on the changes in properties of the ZSM-5 zeolite were investigated.

In the preliminary experiments, it was revealed that the zeolite samples treated by the CCS method using DEMS and TPS were inactive in the trans-alkylation 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 SiO_2 units in response to the CCS treatment. Figs. 2 and 3 show the NH_3-TPD spectra and the benzene adsorption isotherms of the powdery zeolites prior to and after CCS treatment using DEMS and TPS. In the NH_3-TPD spectra, the desorption spectra of NH_3 above 600 K corresponds to the desorption of NH_3 from strong acid sites.

The amount of NH_3 desorbed from the strong acid sites of the zeolites after the CCS treatment decreased as compared with the fresh sample. Because the molecular size of NH_3 was much smaller than the pore diameter, NH_3 molecules could pass through the positions in pores where SiO_2 units were formed by the CCS method. Accordingly, the decrease in the number of acid sites represents the number of acid sites covered by SiO_2 units. As shown in Fig. 2, the sample treated by DEMS exhibited a marked decrease in the number of acid sites as compared with the sample treated by TPS. This result indicates that the number of acid sites deactivated by the CCS method depended on the molecular size of the silane compounds used in the method.

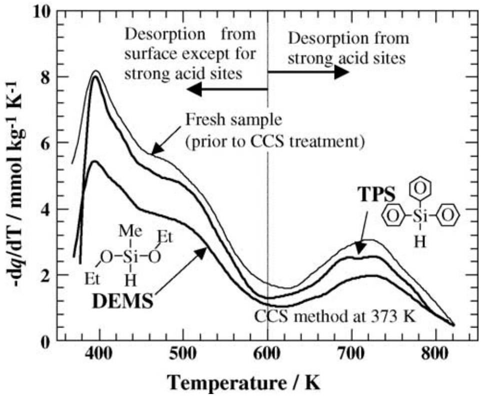

Fig. 2. Changes in the NH_3-TPD profiles of ZSM-5 zeolite caused by SiO_2 unit formation on the acid sites.

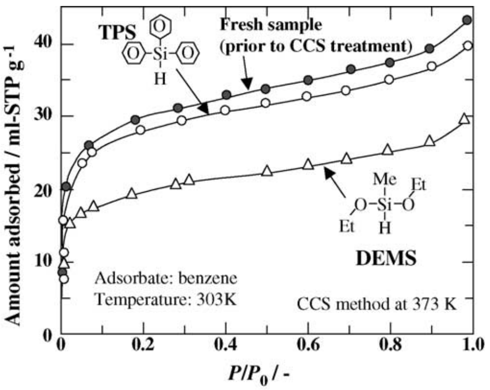

Fig. 3. Adsorption isotherms of benzene on ZSM-5 zeolites prior to and after CCS treatment.

In the zeolite after CCS treatment using DEMS, the amount of adsorbed benzene decreased significantly as compared with the zeolites prior to and after the CCS treatment using TPS. Because the molecular size of benzene is almost equal to the pore diameter of ZSM-5 zeolites, benzene molecules could not diffuse through the position of the pores where SiO_2 units were formed by the CCS method. Accordingly, the decrease in the amount of adsorbed benzene corresponded to the pore space completely blocked by SiO_2 units for benzene diffusion. Therefore, the decrease in the amount of benzene adsorbed within the zeolite after the CCS treatment also depended on the molecular size of the silane compounds.

These differences in the properties of the zeolites after CCS treatment using DEMS and TPS observed in Figs. 2 and 3 can be ascribed to the difference in the location of acid sites covered by the SiO_2 units. Because the molecular size of DEMS was smaller than that of micropores within the ZSM-5 zeolite, DEMS could diffuse into the micropores of zeolite, and the acid sites in the pore as well as on the outer surface of the zeolite were deactivated by the CCS method. On the contrary, since the molecular size of TPS was larger than that of the micropore, TPS could not penetrate the micropore, leading to the selective adsorption of TPS on acid sites on the outer surface of the zeolite.

As a result, the selective adsorption of TPS occurred on the acid sites on the outer surface of the zeolite crystal due to its large molecular size, and the location of acid sites of the ZSM-5 zeolite could be controlled by the CCS method with silane compounds of different molecular sizes.

3.2. Conversion of methanol to olefins using the ZSM-5 catalytic membrane

To prevent conversion of methanol to paraffin and aromatics on the feed side of the membrane, it was considered that the acid sites on the surface of the ZSM-5

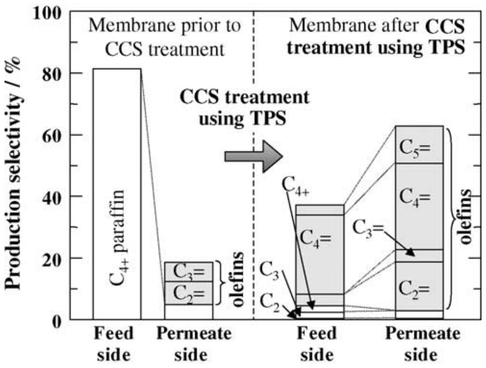

Fig. 4. Production selectivity for the reaction of methanol from the feed and permeate sides of the membrane.

zeolite membrane facing the feed side should be selectively deactivated by the CCS method employing TPS.

Fig. 4 shows the typical production selectivity of the MTO reaction using the ZSM-5 zeolite membranes prior to and after the CCS treatment using TPS. In the membranes prior to the CCS treatment, though olefins were obtained in the products recovered from the permeate side, the production selectivity of paraffin in the feed side was much higher than that of olefin in the permeate side. The paraffin production in the feed side resulted from the conversion of methanol to paraffin over acid sites on the outer surface of the membrane facing the feed side. Moreover, the chain length of the produced paraffin from the feed side was longer than that of olefin and paraffin observed in the permeate side. These resulted from the non-shape-selective reaction of the hydrocarbons over the acid sites on the surface of the membrane facing the feed side.

In contrast, the production selectivity of the paraffin was extremely decreased in the feed and permeate sides when using the zeolite membrane treated by the CCS method using TPS. Moreover, the olefins selectivity in the permeate side was higher than that in the feed side. These results indicate that the reaction in series of methanol over the acid sites on the feed side of the zeolite membrane was inhibited. In other words, because the acid sites on the surface facing the feed side were selectively deactivated by the CCS method using TPS, the paraffin production from methanol was inhibited in the feed side. Accordingly, the methanol that diffused into the zeolite membrane was converted into olefins, and the olefins selectivity was increased on the permeate side.

3.3. *Dependency of olefin yield on methanol conversion*

Fig. 5 shows the relationship between methanol conversion and the molar fraction of olefins in products recovered from the permeate side of the zeolite membrane. The data from a fixed bed-type reactor and the zeolite membrane prior to the CCS treatment were also plotted for comparison. Compared with the fixed bed-type reactor, the zeolite membrane exhibited high selectivity for olefins, especially at higher conversions of methanol. Moreover, by applying the CCS method to the zeolite membrane, the selectivity of the olefins was improved by almost 10%. This improvement resulted from the selective deactivation of the acid sites on the outer surface of the zeolite membrane, which could inhibit the production of paraffin and aromatics.

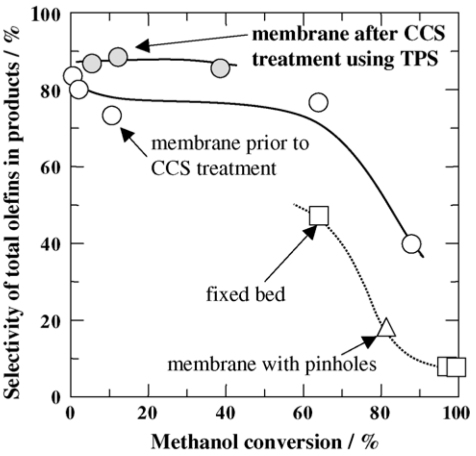

Fig. 5. Relationship between methanol conversion and the selectivity of olefins obtained from the permeate side of the membrane.

4. 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 catalytic activity for the reaction of methanol and high selectivity of olefins, which is the intermediate species in the reaction. However, an undesirable reaction of methanol to paraffin and aromatics proceeded on the outer surface of the membrane (feed side). To prevent the production of paraffin and aromatics, the location of the acid site of the ZSM-5 zeolite membrane was controlled by the CCS method using silane compounds with different molecular diameters (di-ethoxy-methyl silane; DEMS and tri-phenyl silane; TPS). By employing TPS as a SiO_2 unit-forming agent, the acid sites on the outer surface of the 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) by the CCS method led to a decrease in the production of paraffin and aromatics on the feed side. The olefins selectivity reached 90% at a methanol conversion of 40%.

Acknowledgements

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