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Study on Mo/HZSM-5 catalysts modified by bulky aminoalkyl-substituted silyl compounds for the selective methane-to-benzene (MTB) reaction

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Abstract

The methane dehydroaromatization reaction was carried out over SiO_2-modified Mo/HZSM-5 catalysts at 1023 K under 0.3 MPa with 2700 $ml\,g^{-1}\,h^{-1}$ of 6% H_2 added methane. The molecular tuning effect of silanation treatment for HZSM-5 crystals was studied using various silyl compounds, including 3-aminopropyl-triethoxysilane (APTES), 3-aminopropyl-trimethoxysilane (APTMS), *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (TESPDHI), triphenylsilylamine (TPSA), *N*-propyl-triethoxysilane (PTES), and tetraethoxysilane (TEOS). It was found that the optimum addition (0.5 wt% as SiO_2) of basic group-substituted bulky silyl compounds such as APTES, APTMS and TESPDHI resulted in the fine tuning of the external microporous apertures of HZSM-5 having ca. 5.0 Å diameter similar to that of MCM-22, and improve the benzene selectivity of above 90% (benzene + toluene) in the methane dehydroaromatization reaction on 6 wt% Mo/HZSM-5 catalysts due to the marked suppression of naphthalene and coke formation. In contrast, the other bulky silyl compounds are not effective for the surface modification of Mo/HZSM-5 in the MTB reaction. The IR of pyridine adsorption studies revealed that the surface Brønsted acid sites of HZSM-5 was selectively transformed to Lewis acid sites by the treatment of the selected silyl agents such as APTES, APTMS, and TESPDHI, resulting in highly stable and selective catalytic performance of Mo/HZSM-5 in the MTB reaction.

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Keywords: Methane-to-benzene (MTB) reaction; Fine molecular tuning; Silanation treatment; Mo/HZSM-5

1. Introduction

Methane dehydroaromatization is considered one of the most important reactions from the standpoint of utilization of methane derived from natural gas, biogas, and methane hydrate, producing benzene and naphthalene as useful petrochemical feedstocks for plastics and fibers and hydrogen for fuel cell society, respectively. First, the process of aromatization of methane over Mo-modified ZSM-5 was described Wang et al. in 1993 [1]. We have previously reported that Mo_2C/HZSM-5 and Re/HZSM-5 catalysts exhibit high activity and selectivity toward benzene and naphthalene [2–6]. Molybdenum carbide or rhenium metal activates methane converting to CH_x species, which are catalytically condensed on the Brønsted acid sites of internal ZSM-5 micropores, producing aromatics such as benzene, toluene, and naphthalene. The product distribution is managed by molecular shape selectivity due to the external pore apertures (ca. 5 Å diameter equivalent to benzene molecule) of zeolite supports, such as ZSM-5 and MCM-22 [6].

Nevertheless, the Mo/HZSM-5 catalysts are readily deactivated within a few hours of time on stream in the methane dehydroaromatization reaction owing to the serious coke deposition by reducing the external pore apertures of HZSM-5 zeolite support (Scheme 1). In an attempt to overcome this poisoning problem, we investigated the effects of adding a few percent of H_2 or CO_2 to the methane feed, and found that it significantly promoted the catalyst performance in maintaining activity and product selectivity as the result of the efficient removal of coke under the working conditions [4,5,7]. Moreover, we investigated the effects of adding noble metal (Pt and Rh) to Mo/HZSM-5 catalyst to promote coke removal under the H_2 added methane feed and to improve catalyst stability [8].

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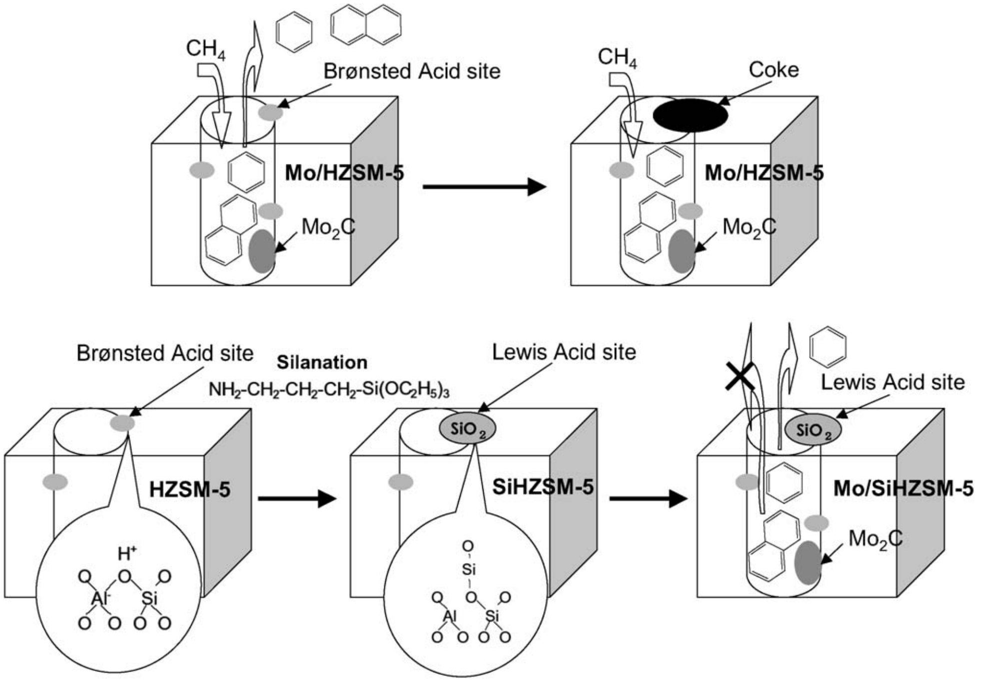


Scheme 1. The pictorial representation of (1) site blocking with coke which is formed from the condensed aromatic products at the surface Brønsted acid sites of Mo/HZSM-5 catalyst and (2) the selective silanation treatment of HZSM-5 by the bulky aminopropyl-triethoxysilane (APTES) at the surface Brønsted acid sites which are converted to Lewis acid sites on the calcinations. This makes a fine tuning of the external pore apertures of HZSM-5 and Mo/HZSM-5 for the selective MTB reaction.

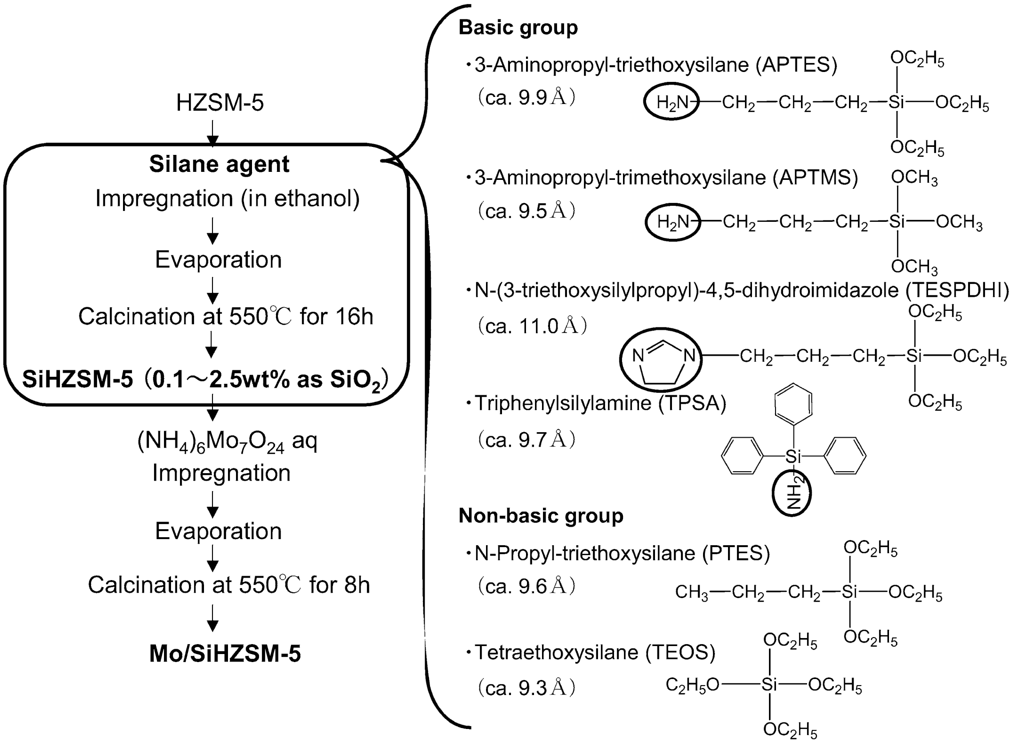
Brønsted acid sites on the external zeolite surfaces have been implicated in many catalytic reactions with lower selectivity and catalytic performance. Such sites are easily accessed by the deeply condensed aromatic products to form coke, causing catalyst deactivation [9,10]. Iglesia et al. reported that a silica-modified Mo/HZSM-5 catalyst promotes the selective hydrocarbon reaction due to the neutralization of the external Brønsted acid sites by amino-substituted silyl compounds [11]. The steric restrictions within zeolite channels inhibit the formation of large activated complexes and hinder the formation of polynuclear aromatics and of alkylated benzenes larger than durene. However, Mo/HZSM-5 catalysts form considerable amounts of naphthalene and detectable amounts of larger aromatics from CH_4 despite the expected shape selectivity [12, 13]. The elimination of any external Brønsted acid sites that are potentially responsible for these nonselective pathways may inhibit the formation of deactivating carbon residues and increase the selectivity to benzene. This study addresses the molecular tuning of external pore apertures of HZSM-5 and suppression of the external Brønsted acid sites modified by the selected basic group-substituted silyl compounds, along with the catalytic behavior of Mo/HZSM-5 with or without specific external silanation treatment for the methane dehydroaromatization reaction. Such large organosilane molecules with basic groups cannot enter into the internal ZSM-5 channels while they interact with the external Brønsted acid sites and provide fine-tuning of the external pore apertures by atomic silicate after calcination. The results reported here show that fine-tuning of the external apertures of HZSM-5 by limited amount of the selected bulky silyl compounds results in the effective promotion of benzene selectivity in hydrocarbon products (>90%) and stable performance due to the crucial suppression of naphthalene and coke formation in methane dehydroaromatization on the SiO_2-modified Mo/HZSM-5 catalysts, as shown in Scheme 1.

2. Experimental

2.1. Catalyst preparation

2.1.1. Silanation treatment of HZSM-5

Silica-modified HZSM-5 zeolite was prepared by immersing HZSM-5 (calcinated NH_4ZSM-5 [Tosho; Si/Al = 20]), into an ethanol solution (150 cm^3) containing 3-aminopropyl-triethoxysilane (APTES), 3-aminopropyl-trimethoxysilane (APTMS), *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (TESPDHI), triphenylsilylamine (TPSA), *N*-propyl-triethoxysilane (PTES), and tetraethoxysilane (TEOS) and subsequently evaporating the ethanol solvent at 313 K [11,14,15]. Then the samples were treated at 823 K for 16 h in air to decompose the organosilane precursors and form the silica-modified HZSM-5 (0.1–2.5 wt% as SiO_2), as indicated in Scheme 2 (silanation treatment procedure and molecular structures of silyl compounds). The large size of the organosilane molecules APTES, APTMS, TESPDHI, TPSA, PTES, and TEOS prevents the titration of acidic OH groups within zeolite channels; only the external surfaces react with these bulky silica precursors. In addition, APTES, APTMS, TESPDHI, and TPSA have strongly basic amino and imidazole groups, leading to significant adsorption on the external surface acid sites of zeolites.



Scheme 2. Silanation treatment procedure and molecular structures of silyl compounds.

2.1.2. *Preparation of Mo-supported ZSM-5 and MCM-22 catalysts*

The 6 wt% Mo/HZSM-5 and 6 wt% Mo/HMCM-22 samples were prepared by the conventional impregnation method using NH_4-ZSM-5 (Tohso; Si/Al = 20) or NH_4-MCM-22 (Tohso; Si/Al = 14) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ water solution. The 6 wt% Mo/silica-modified HZSM-5 was prepared by the similar impregnation method using silica-modified HZSM-5 calcined after the silanation treatment with a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution. The samples were dried by a rotary evaporator, and calcined in a dry air at 823 K for 8 h. The resulting Mo/HZSM-5 samples were precarburized by the temperature-programmed heating at a rate of 5 $K\,min^{-1}$ up to 973 K (where it was maintained for 2 h) under the $CH_4 + 4H_2$ mixed gas, which were subjected to the methane dehydroaromatization reaction at 1023 K and 3 atm of methane + 6% v/v H_2, as shown in the literature.

2.2. *Catalytic reaction*

Catalytic tests in the methane-to-benzene (MTB) reaction were carried out under 3 atm of methane with or without H_2 addition in a continuous-flow system with a quartz reactor charged with 0.3 g of catalyst pellets of 20–42 mesh, as has been reported previously [8]. The feed gas mixture (99.9% pure, Sumitomo Seika) of 90% CH_4 and 10% Ar was introduced into the reactor at 15 $ml\,min^{-1}$ (space velocity of methane = 2700 $ml\,g\text{-cat.}^{-1}\,h^{-1}$) through a mass flow controller. Hydrocarbon products including C_2–C_4 alkanes (and/or alkenes) and condensable C_6–C_{12} aromatics, such as benzene, toluene, xylene, and naphthalene, were analyzed by on-line gas chromatography with flame ionization detection on a Porapak-P column using a six-way sampling valve heated to 533 K and the on-line TCD GC for H_2, Ar, and CH_4 on an activated carbon column. Using an internal standard analyzing method of 10% v/v in the feed gas of methane with or without H_2, the conversion of methane and formation rates of hydrogen and hydrocarbon products were evaluated. Formation rates of hydrocarbon products were also calculated and expressed in terms of carbon base.

2.3. *Characterization*

The identification of zeolites based on their porous structures was achieved by X-ray diffraction using a Rigaku MiniFlex. BET surface areas and pore volumes were determined by nitrogen adsorption using a YUASA AUTOSORB-6 and a Bel Japan Belsorp 18. Micropore size distributions were measured by Ar adsorption using a Bel Japan Belsorp 28 and calculated by the HKSF method [16–18]. The IR spectra for the framework vibration were recorded on a FTIR spectrometer (JASCO FT/IR-420) with a resolution of 1 cm^{-1} at room temperature. The sample was pressed into a self-supporting thin wafer and placed in a quartz IR cell with CaF_2 windows. Before the measurements, each sample was dehydrated under vacuum at 673 K for 2 h. The IR spectra of chemisorbed pyridine on the protonated ZSM-5 zeolites were also measured at room temperature. The adsorption of pyridine was carried out at 423 K for 1 h, and then evacuated at 523 K for 0.5 h to remove the excess pyridine and weakly adsorbed pyridine [19,20].

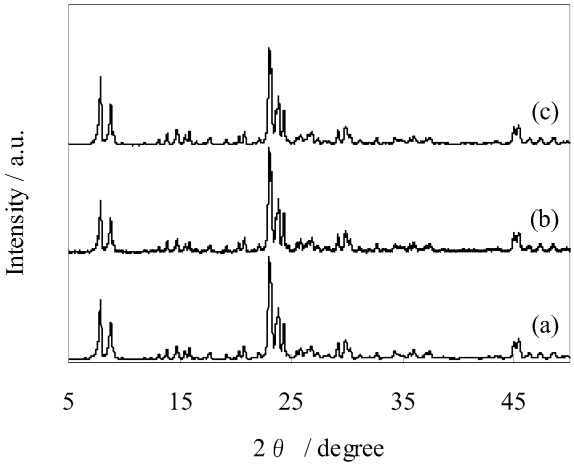


Fig. 1. Powder X-ray diffraction patterns of HZSM-5 and silica-modified HZSM-5 prepared by the silanation treatment using the different amount of APTES. (a) HZSM-5, (b) Si(0.5 wt%)HZSM-5, (c) Si(2.5 wt%)HZSM-5.

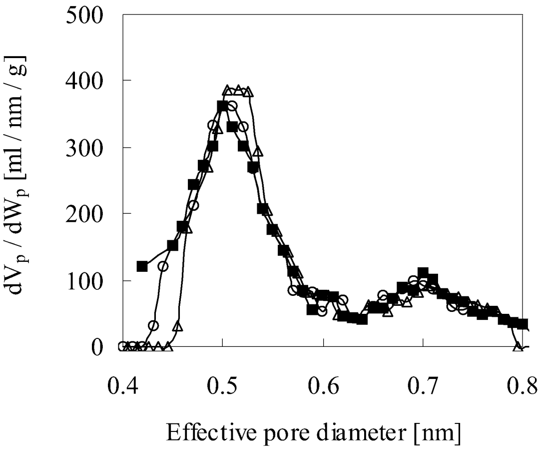


Fig. 2. Micropore size distributions for HZSM-5 and silica-modified HZSM-5 prepared by the silanation treatment using the different amount of APTES derived from Ar adsorption isotherm. (■) HZSM-5, (○) Si(0.5 wt%)HZSM-5, (△) Si(2.5 wt%)HZSM-5.

3. Results and discussion

3.1. *Silanation treatment of HZSM-5 by bulky aminopropyl-substituted silyl compounds*

Mo/HZSM-5 catalyst is very active for the methane dehydroaromatization reaction, but it is gradually deactivated during the reaction due to the coke deposition on the catalyst. Our previous study suggested that the heavy aromatic products, such as naphthalene, can be adsorbed and condensed on the Brønsted acid sites located on the external surface and can be a source of coke. The external Brønsted acid sites transform into inactive Lewis acid sites when treated by the selected bulky silyl compounds to prevent the adsorption of naphthalene [2,3,5]. Accordingly, silanation treatment on the external surface of ZSM-5 may be a promising means of suppressing coke deposition and stabilizing catalyst performance.

We studied the silanation treatment of ZSM-5 crystals, which may affect the porous structure of the zeolite. Fig. 1 shows the powder X-ray diffraction patterns of ZSM-5 samples treated by varying amounts of 3-aminopropyl-triethoxysilane (APTES). For all the resulting samples after calcination at 823 K, the XRD patterns and their intensity were not changed with or without the silanation treatment, and no additional peaks except those corresponding to HZSM-5 were observed.

The micropore size distribution of the silica-modified zeolite was measured by the Ar adsorption technique using the HKSF method; the results are shown in Fig. 2. For all of the samples, the effective diameters were almost equivalent to those of the original HZSM-5 regardless of the silanation treatment. The silyl compounds used in this study are larger (9–11 Å molecular diameter) than the zeolite pores (5.5 Å diameter), because the Brønsted acid sites in the pores are active for the methane dehydroaromatization reaction. Only those on the external surface should be modified by the basic group-substituted silyl compounds. The pore size at the entrance can be changed by this treatment because of SiO_2 formation at the vicinity of the Brønsted acid sites; however, the data obtained by the Ar adsorption technique indicated that the pore size distributions of HZSM-5 are apparently not changed for the samples with or without silanation treatment by 3-aminopropyl-triethoxysilane (APTES). Thus, there is no change in the original micropores in HZSM-5 by the silanation treatment, possibly with small changes for the external pore apertures, which may reflect the product selectivities in methane dehydroaromatization on Mo/HZSM-5 with or without the silanation treatment. The BET surface areas and pore volumes of silane-modified zeolites are listed in Table 1. BET surface areas and pore volumes remained essentially unchanged, indicating no internal modification of the HZSM-5 caused by the silanation treatment by APTES.

Table 1
BET surface area and pore volume of HZSM-5 and Si-modified HZSM-5 treated by APTES

No. sample	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
HZSM-5	438	0.15
Si(0.5 wt%)-modified HZSM-5	433	0.15
Si(2.5 wt%)-modified HZSM-5	419	0.15

To investigate the surface structures and chemistry of the Si-modified ZSM-5, the samples were measured by the IR spectroscopy. As shown in Fig. 3, in the 4000–3000 cm^{-1} region, the HZSM-5 zeolite after the silanation treatment with APTES clearly showed two IR peaks at ca. 3613 and 3779 cm^{-1}. These IR peaks can possibly be assigned to the acidic bridged OH of Si(OH)Al and isolated silanol groups, respectively. The acidic-bridged OH peak was relatively weakened after the treatment by APTES. Furthermore, the IR study of pyridine adsorption revealed (Fig. 4) that the IR spectra of pyridine-adsorbed HZSM-5 zeolite and 0.5 wt% silica-modified zeolite [Si(0.5 wt%)HZSM-5] exhibited a characteristic change in the IR bands in the 1650–1400 cm^{-1} region. The original HZSM-5 zeolite exhibited several peaks due to Lewis acid site–bound pyridine (L: 1458 cm^{-1}) and pyridinium ion on Brønsted acid sites (B: 1543 cm^{-1}), respectively. The Brønsted acid peak was relatively weakened; as a result, the Lewis acid site peak at

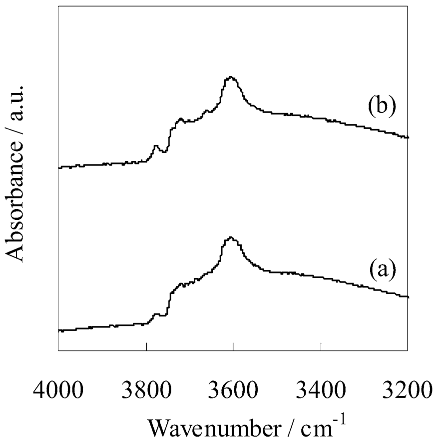


Fig. 3. IR spectra of HZSM-5 and silica-modified HZSM-5 prepared by the silanation treatment using APTES. (a) HZSM-5, (b) Si(0.5 wt%)HZSM-5.

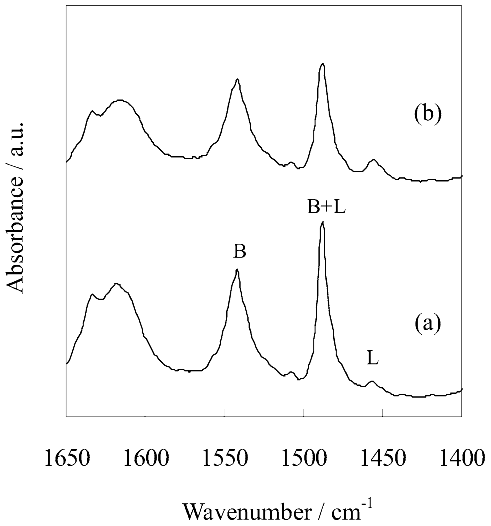
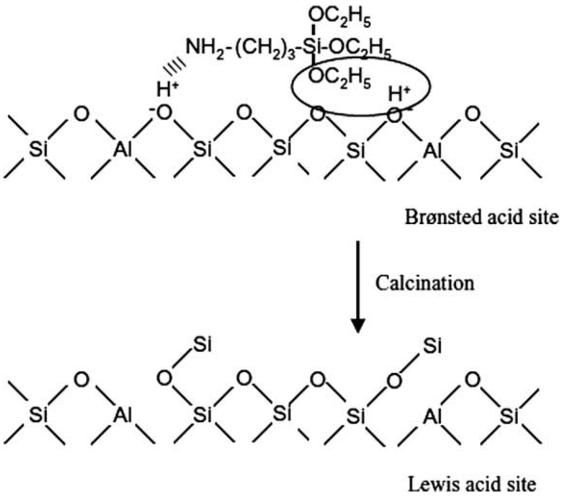


Fig. 4. IR spectra of pyridine adsorbed on HZSM-5 and silica-modified HZSM-5 prepared by the silanation treatment using APTES. (a) HZSM-5, (b) Si(0.5 wt%)HZSM-5.

1458 cm^{-1} was slightly enhanced for the sample after the silanation treatment by APTES. These results indicated that only the external surface Brønsted acid sites were modified, being transformed to Lewis acid sites by the silanation treatment of HZSM-5 (Scheme 3). In addition, it seems that other bulky basic group-substituted silyl compounds, such as APTMS and TESPDHI, may have effectively interacted with the surface Brønsted acid sites of HZSM-5 similar to APTES. Moreover, IR spectroscopy was used to investigate the interaction between the silane compound and the surface Brønsted acid sites in silanation treatment in the samples. As shown in Fig. 5, the clear IR peak at 3613 cm^{-1} derived from Brønsted acid sites was observed in the fresh HZSM-5 (a). After drying the sample at 393 K, this peak was decreased, and the peaks derived from methylene group (2985, 2910, 1447, 1388 cm^{-1}) and methyl group (1502 cm^{-1}) appeared. Finally, after calcination (c), the peaks derived from methylene and methyl groups were diminished, and the peak derived from the Brønsted acid sites reappeared at 3613 cm^{-1}. These results demonstrate the interaction between bulky basic group-substituted silyl compounds and surface Brønsted acid sites.



Scheme 3. The manifestation process of Lewis acid sites by silane agents with a base group.

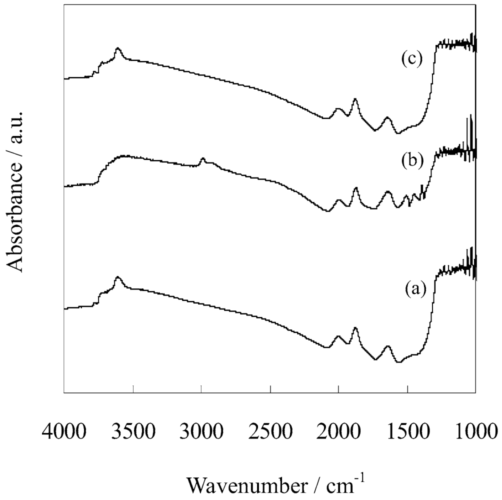


Fig. 5. IR spectra of HZSM-5, silica as-modified HZSM-5 (after dry) and silica-modified HZSM-5 (after calcination). (a) HZSM-5, (b) silica as-modified HZSM-5 (after dry), (c) silica-modified HZSM-5 (after calcination).

3.2. *Catalytic activity and stability of the methane-to-benzene reaction*

In the methane dehydroaromatization reaction, molybdenum carbide active for methane conversion to CH_x ($x = 1–3$) and the condensation of the CH_x species proceeded on the internal Brønsted acid sites in the micropores of HZSM-5, producing such aromatics as benzene, toluene, and naphthalene due to the shape-selectivity effect of the external pore apertures [2,3,5,6, 11]. This shows that it is possible to control the product selectivity by changing the aperture size of zeolite.

Methane conversion and product selectivity at 1023 K under 0.3 MPa over Mo/HMCM-22 and Mo/HZSM-5 catalysts in the methane dehydroaromatization reaction with or without the addition of H_2 to methane are listed in Table 2. XRD

Table 2
CH_4 conversion and selectivity to hydrocarbon products over Mo/HZSM-5 and Mo/HMCM-22 catalysts

Catalyst	H_2 addition (%)	CH_4 conversion (%)	Hydrocarbon selectivity (%, carbon base)			
			C_2	Benzene	Toluene	Naphthalene
Mo/HZSM-5	0	8.9	5.9	70.0	4.8	19.3
Mo/HZSM-5	6	8.0	7.7	60.6	5.1	26.6
Mo/HMCM-22	0	10.0	5.8	86.5	7.4	0.3
Mo/HMCM-22	6	8.4	6.9	85.4	7.7	0

Note. Data was taken after 3 h at 1023 K, 0.3 MPa, and 2700 ml h^{-1} g^{-1} CH_4 SV, 6% v/v H_2 addition.

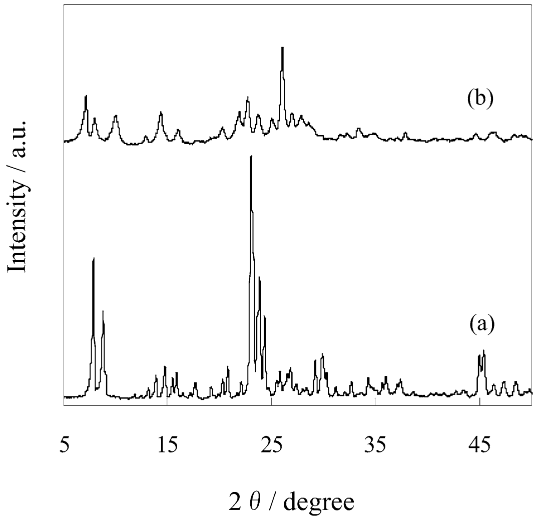


Fig. 6. Powder X-ray diffraction patterns of HZSM-5 and HMCM-22. (a) HZSM-5, (b) HMCM-22.

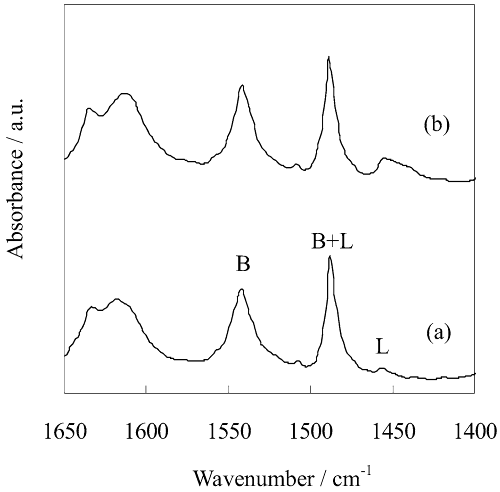


Fig. 7. IR spectra of pyridine adsorbed on HZSM-5 and HMCM-22. (a) HZSM-5, (b) HMCM-22.

measurements confirm that the HZSM-5 and HMCM-22 zeolites used in this study had MFI and MWW structures, respectively (Fig. 6). The product selectivity over Mo/HZSM-5 was as follows: in pure methane aromatization, 70.0% benzene, 19.3% naphthalene, 4.8% toluene, and 5.9% C2 compounds (C_2H_4 and C_2H_6); in 6% H_2 addition, 60.6% benzene, 26.6% naphthalene, 5.1% toluene, 7.7% C2 compounds (C_2H_4 and C_2H_6), and a few percent of C3 compounds (C_3H_6 and C_3H_8). In contrast, the product selectivity over Mo/HMCM-22 was as follows: in pure methane aromatization, 86.5% benzene, 0.3% naphthalene, 7.4% toluene, and 5.8% C2 compounds (C_2H_4 and C_2H_6); in 6% H_2 addition, 85.4% benzene, 6.9% toluene, and 7.7% C2 compounds (C_2H_4 and C_2H_6). Naphthalene was hardly observed. MCM-22 zeolite is known to have smaller pore size (4.0 × 5.5 Å, 4.1 × 5.1 Å) than ZSM-5 zeolite (5.3 × 5.6 Å, 5.1 × 5.5 Å). Accordingly, larger condensed aromatics, such as naphthalene (ca. 5 × 8 Å), are negligibly produced in the reaction. Although naphthalene can be produced not only in the supercage (7.1 × 7.1 × 18.2 Å), but also on the external surface with the same Brønsted acid sites, the reaction over Mo/HMCM-22 provides 90% product selectivity for benzene and toluene, due to the molecular shape selectivity of their external pore apertures. To investigate the acidities of HZSM-5 and HMCM-22 zeolites, we measured the IR spectra of pyridine-adsorbed samples. As shown in Fig. 7, the Brønsted acidities of HZSM-5 and HMCM-22 are on same level; therefore, each zeolite aperture can affect the catalytic performance of Mo/HZSM-5 and Mo/HMCM-22 in the methane dehydroaromatization reaction.

It is interesting to note that product selectivity on the Mo/HZSM-5 catalysts is greatly affected by silanation treatment of the HZSM-5 support. Table 3 gives CH_4 conversions and product selectivities over the Mo/HZSM-5 catalysts with or without the 0.5 wt% silica modification using various precursor silyl compounds (APTES, APTMS, TESPDHI, TPSA, PTES, and TEOS). Among the bulky silyl compounds, naphthalene formation was effectively suppressed to almost zero, and benzene and toluene selectivity increased up to 90% on the carbon base only for the modified Mo/HZSM-5 using APTES, APTMS, and TESPDHI with the basic groups such as 3-amino and dihydroimidazole-substituted propyl in their molecules. The product selectivity in the reaction resembles that on Mo/MCM-22, which has smaller pore apertures than ZSM-5. Moreover, other bulky silyl compounds, such as PTES and TEOS, without the basic group in the molecule showed no critical affection in the product selectivity of the reaction, even when compared with those over the original Mo/HZSM-5. TPSA with an amino group attached directly to silyl moiety produced a slight change in product selectivity, similar to that on the modified catalysts by PTES and TEOS. This is related to the bulkiness of three phenyl groups in preventing the chemical interaction between the amino group and external Brønsted acid sites of HZSM-5. Y. Xu et al. reported that the silanation of Mo/HZSM-5 with TEOS showed higher activity and stabil-

Table 3
CH_4 conversion and product selectivity over Mo/HMCM-22, Mo/HZSM-5, and Mo/Si-modified HZSM-5 prepared by various kinds of silyl compounds

Catalyst	Conversion (%)[a]	Hydrocarbon selectivity (%, carbon base)			
		C_2	Benzene	Toluene	Naphthalene
Mo/HMCM-22	8.2	7.7	85.4	6.9	0
Mo/Si(0.5 wt%)HZSM-5[b] APTES	6.0	12.5	68.5	18.0	1.0
Mo/Si(0.5 wt%)HZSM-5[b] APTMS	6.7	9.3	73.5	13.4	3.8
Mo/Si(0.5 wt%)HZSM-5[b] TESPDHI	7.5	7.6	77.3	13.0	2.1
Mo/Si(0.5 wt%)HZSM-5[b] TPSA	5.9	6.9	76.8	4.8	11.5
Mo/Si(0.5 wt%)HZSM-5[b] PTES	6.8	7.6	77.8	4.3	10.3
Mo/Si(0.5 wt%)HZSM-5[b] TEOS	6.5	6.6	75.7	4.2	13.5
Mo/HZSM-5	7.7	9.4	60.3	4.1	26.2

[a] Data was taken after 4 h at 1023 K, 0.3 MPa, 2700 ml h^{-1} g^{-1} of CH_4 SV, 6% v/v H_2 addition.
[b] 6 wt% Mo-supported SiO_2-modified HZSM-5 catalysts prepared by various kinds of silyl compounds.

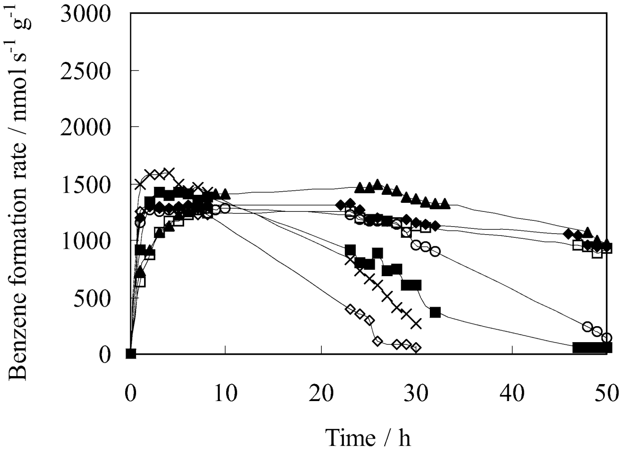


Fig. 8. Time course of benzene formation rate in the methane dehydroaromatization reaction over 6 wt% Mo/HZSM-5 and 6 wt% Mo-supported SiO_2-modified HZSM-5 prepared by the silanation treatment using various kinds of silyl compounds. The reaction was performed under conditions of 1023 K, 0.3 MPa, and 2700 ml g^{-1} h^{-1} of CH_4 space velocity with 6% v/v H_2 addition. (○) Mo/HZSM-5, (◆) Mo/SiO_2(0.5 wt%; APTES)HZSM-5, (□) Mo/SiO_2(0.5 wt%; APTMS)HZSM-5, (▲) Mo/SiO_2(0.5 wt%; TESPDHI)-HZSM-5, (■) Mo/SiO_2(0.5 wt%; TPSA)HZSM-5, (◇) Mo/SiO_2(0.5 wt%; PTES)HZSM-5, (×) Mo/SiO_2(0.5 wt%; TEOS)HZSM-5.

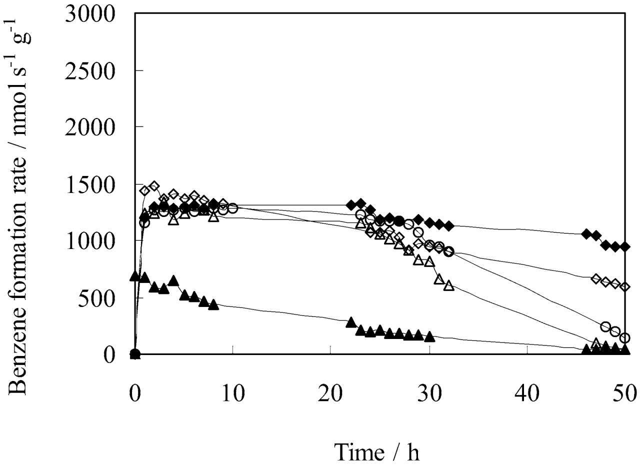


Fig. 9. Time course of benzene formation rate over 6 wt% Mo/HZSM-5 and 6 wt% Mo-supported SiO_2-modified HZSM-5 catalysts prepared by the silanation treatment using various amount of APTES. The reaction was performed under conditions of 1023 K, 0.3 MPa, and 2700 ml g^{-1} h^{-1} of CH_4 space velocity with 6% v/v H_2 addition. (○) Mo/HZSM-5, (◇) Mo/SiO_2-(0.25 wt%)HZSM-5, (◆) Mo/SiO_2(0.5 wt%)HZSM-5, (△) Mo/SiO_2(0.75 wt%)HZSM-5, (▲) Mo/SiO_2(2.5 wt%)HZSM-5.

ity [21], but the silanation method used was chemical vapor deposition (CVD).

Fig. 8 shows the time course of benzene formation over Mo/HZSM-5 modified by various silyl compounds (APTES, APTMS, TESPDHI, TPSA, PTES and TEOS). TPSA, PTES, and TEOS did not exhibit positive effects like APTES, APTMS and TESPDHI did. Fig. 8 shows that the catalyst had better stability of catalytic performance in the reaction when APTES, APTMS, and TESPDHI were used for the silanation treatment of HZSM-5. These silyl compounds, which have molecules larger than the zeolite pores (ca. 9–11 Å vs ca. 5.0–5.5 Å), cannot be accessible to the internal zeolite pores. Thus, Brønsted acid sites located on the external surface of HZSM-5 are available to interact uniformly with the basic groups (amino and imidazole) of the silyl compounds. It has been suggested previously that adsorption of naphthalene causes coke formation on the surface Brønsted acid sites of zeolite [4–6,11,12]. It is reasonable to assume that such catalyst deactivation due to coke was effectively suppressed and that the catalytic performance of the silica-modified Mo/HZSM-5 was improved by the selective silanation treatment using APTES, APTMS, and TESPDHI.

CH_4 conversion and product selectivity were studied over the silica-modified Mo/HZSM-5 treated by changing the amount of APTES. As shown in Table 4, the naphthalene selectivity was greatly decreased by the silanation treatment with 0.25 wt% SiO_2 of APTES, whereas the benzene selectivity was effectively increased. By increasing the amount of APTES, the resulting catalysts gave similar product selectivity in the reaction, whereas the conversion of methane to benzene decreased substantially, possibly due to the excess covering of silicate layers on the HZSM-5 surface. Even 0.25 wt% SiO_2 as the optimum amount of APTES greatly suppressed naphthalene formation; this amount was sufficient to form 1–2 layer of silica on the external surface of the HZSM-5 crystal. In addition, Lercher et al. reported that about 53–76% of external surface Brønsted acid sites were removed, depending on the cycles of the treatment with TEOS [22]. However, the amount of TEOS for SiO_2 was high, and the removal of external sur-

Table 4
CH_4 conversion and product selectivity over Mo/HZSM-5 treated by various amount of APTES

Catalyst	Conversion (%)[a]	Hydrocarbon selectivity (%, carbon base)			
		C_2	Benzene	Toluene	Naphthalene
Mo/HZSM-5	7.7	9.0	60.7	4.1	26.2
Mo/Si(0.1 wt%)HZSM-5[b]	7.0	7.1	70.9	4.3	17.7
Mo/Si(0.25 wt%)HZSM-5[b]	6.9	8.3	78.5	12.0	1.2
Mo/Si(0.5 wt%)HZSM-5[b]	6.0	9.5	74.5	15.2	0.8
Mo/Si(0.75 wt%)HZSM-5[b]	5.1	8.1	80.0	11.6	0.3
Mo/Si(2.5 wt%)HZSM-5[b]	4.4	11.0	78.1	10.9	0.0

[a] Data was taken after 5 h at 1023 K, 0.3 MPa, 2700 ml h^{-1} g^{-1} of CH_4 SV, 6% v/v H_2 addition.
[b] 6 wt% Mo-supported SiO_2-modified HZSM-5 catalysts prepared by the silanation treatment using various amount of APTES.

face Brønsted acid sites was not sufficient. Fig. 9 shows the time course of benzene formation over Mo/HZSM-5 treated by various amount of silane (APTES). When modified with the 0.5-wt% silica, the catalyst showed the most stable performance in 50 h of time on stream for the silica-modified Mo/HZSM-5 using 0.5 wt% silica derived from APTES on HZSM-5. These results indicate that the surface of zeolite can be modified uniformly with a small amount of basic group-substituted bulky silyl compounds, but the excess doping of the silyl compounds by 0.75–2.5% SiO_2 may form thicker films of silica, which block the external pores of HZSM-5, reducing the external aperture size, as reflected in decreased methane conversion and increased selectivity of the smaller products, such as C2–C3 hydrocarbons, instead of benzene, toluene, and naphthalene, as shown in Table 4.

4. Conclusion

Based on our findings, the following conclusions can be drawn:

1. The silica-modified Mo/HZSM-5 by the selective bulky silyl compounds greatly improved benzene selectivity to >90% (benzene + toluene), similar to that on Mo/HMCM-22, due to the effective suppression of naphthalene formation and catalytic stability in the methane dehydroaromatization reaction.
2. The silanation treatment is effective only when the Brønsted acid sites on HZSM-5 are reacted selectively with a limited amount of the bulky silyl compounds, such as APTES, APTMS, and TESPDHI, that have a base group (e.g., an amino group) and an imidazole group in their molecules. The optimum addition of APTES to HZSM-5 (0.5 wt% as SiO_2) resulted in a selective methane-to-benzene reaction on the silica-modified Mo/HZSM-5 catalysts and improved the catalytic performance.
3. APTES interacted selectively with the external Brønsted acid sites of HZSM-5, which were converted to Lewis acid sites under calcination in air at 823 K. The resulting silica-modified HZSM-5 exhibited fine-tuning of micropore apertures of HZSM-5 (5.3 × 5.6 Å, 5.1 × 5.5 Å) similar to those of HMCM-22 (4.0 × 5.5 Å, 4.1 × 5.1 Å), which was reflected in >90% selectivity of benzene + toluene without naphthalene formation in the methane aromatization reaction.

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