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Surface modification of zeolites using benzene-1,4-diboronic acid to form gated micropores with mild and photo responsive pore reopening

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ABSTRACT

Regularly arranged pore structures are effective for regulating molecular permeation processes. Microporous zeolite materials are advantageous to manipulate the diffusion of gaseous molecules. Especially, zeolitic membranes are actively utilized in a number of membrane separation processes. Recently, we have reported that some disilylbenzene compounds grafted onto the surfaces of mordenite and ZSM-5 zeolites sealed their micropores to restrict the penetrations of molecular nitrogen, and that the calcination and heated HCl treatment reopened the sealed micropores. This paper reports that the micropores of mordenite and ZSM-5 zeolites were also sealed with the surface modification using benzene-1,4-diboronic acid, and molecular nitrogen cannot permeate into the micropores thus closed. This modification process provided some milder reopening of the sealed micropores such as diluted HCl treatment at room temperature. The reopening process was also successful by the UV irradiation to the solid zeolite samples after the impregnation of photo-acid generator (PAG). The pore reopening of the micropores with photoirradiation in solid phase is a unique technique that will be applicable for some manipulation technologies of gaseous molecules.

1. Introduction

The controls of diffusion and permeation of small molecules are important technologies in chemistry [1–3]. Regularly arranged pore structures are potent components for regulating molecular permeation processes [4–6]. Gating systems and analogs modified on mesoporous materials are actively studied to create various kinds of interesting controlled releases of molecules [7–15]. The microporous structures of zeolite and related materials are also advantageous to manipulate the permeation of small molecules including gaseous molecules, which is not generally accomplished by mesoporous materials. The effective separation processes of gaseous compounds have been achieved using these microporous materials. Zeolitic membranes are representative examples of those practical processes using the microporous materials [16–23]. Some responsive systems of the suppression of gas permeation were also attempted by photo-chromic molecules embedded in their micropore voids [24–26]. However, the complete controls and restrictions of the permeation of small molecules have been scarcely examined.

We recently reported that 1,4-bis(hydroxydimethylsilyl) benzene and the analogous compounds perfectly blocked the penetration of small molecules such as molecular nitrogen into the micropores of zeolite materials [27]. These disilylated molecules formed the crosslinking on the surface of the zeolites to prevent the permeation of small molecules into the micropore efficiently. Calcination or acid treatment removed the blocking disilylbenzene species to reopen the micropores. These processes are repeatable and expected to control the diffusions of gaseous molecules entirely. Although this is the first example of the complete pore gating (close and reopen) of micropores of zeolite materials to the best of our knowledge, the further modifications of these processes are certainly required. Some milder or more sophisticated systems are essential to create some novel manipulation technologies of gaseous small molecules. Especially, heating treatment including calcination for the reopening of the micropores will become some impediments to the practical applications of the pore gating of zeolites. In this paper, we wish to report an advanced stage of the gating system of zeolite micropores. The utilization of benzene-1,4-diboronic acid as an alternative for the disilylated molecules provides the complete sealing and reopening of zeolite micropores. In this system, the reopening process was achieved under milder acidic conditions. Furthermore, it was also found that the photoacid generator that forms the corresponding acid compound by

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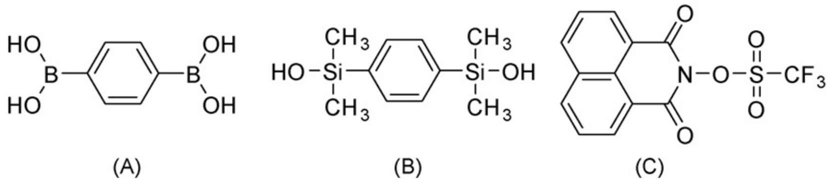

Fig. 1. Chemical structures of benzene-1,4-diboronic acid (**A**), 1,4-bis(hydroxydimethylsilyl)benzene (**B**) and *N*-hydroxynaphthalimide trifluoromethanesulfonate (**C**).

photo-irradiation was effective to reopen the micropore of zeolite materials in solid phase.

2. Experimental

2.1. Materials

Mordenite type zeolites used in this research were obtained as Japan Reference Catalysts (JRC) from Catalysis Society of Japan, JRC-Z-HM20(5) as proton type ($SiO_2/Al_2O_3 = 18.3$) and JRC-Z-M20(1) as sodium type ($SiO_2/Al_2O_3 = 18.5$). ZSM-5 type zeolites, HSZ-840HOA as proton type ($SiO_2/Al_2O_3 = 39$) and HSZ-820NAA as sodium type ($SiO_2/Al_2O_3 = 23.8$) were provided from Tosoh Corporation. Benzene-1,4-diboronic acid (compound **A**) and *N*-hydroxynaphthalimide trifluoromethanesulfonate (a photo-acid generator; compound **C**) were obtained from Aldrich chemical company. 1,4-Bis(hydroxydimethylsilyl)benzene (compound **B**) was purchased from Shin-Etsu Silicones, and their chemical structures are shown in Fig. 1. Other chemicals and reagents are commonly commercially available, and were used without further purification.

2.2. Sealing and reopening processes

Benzene-1,4-diboronic acid (**A**) or 1,4-bis(hydroxydimethylsilyl)benzene (**B**) were grafted onto a zeolite sample in solid phase similar to our previous paper [27]. A typical procedure is described as follows: 2 g of a zeolite example (mordenite or ZSM-5) was immersed in 15 mL of THF solution of a grafting compound (**A** or **B**, 0.2 g), and well mixed at room temperature for 30 min. After removing solvent by evaporation, the zeolite power was put into a Teflon-lined autoclave. After sealing up, the autoclave was heated at 120 or 150 °C for 20 h. The recovered solid was washed with THF twice (100 mL each) for removing the unreacted boron or silane compounds, and finally dried at 120 °C for 12 h.

The reopening processes of the modified zeolite materials were achieved by various methods. Calcination treatment was carried out at 500 °C for 6 h. The treatment with HCl solution was performed as follows: 0.5 g of a modified zeolite was soaked in 500 mL of from 0.2 to 2 M HCl aqueous solution (obtained from 33% HCl solution and deionized water), and the resulting suspension was stirred at room temperature. After filtration, the solid sample was dried at 80 °C for 12 h. The treatment with photo-acid generator and the related processes were carried out as follow: 1 g of a modified zeolite sample was immerged in 15 mL of dichloromethane dissolving 0.1 g of *N*-hydroxynaphthalimide trifluoromethanesulfonate (**C**) as photo-acid generator for 30 min. After removing volatiles under reduced pressure using rotary evaporator, the obtained solid was spread on the Pyrex glass plate (3 mm thick) as thin as possible. The thinness of this powder was less than 1 mm. This thinned powder was sandwiched between two Pyrex glass plates and these two glass plates were secured with clips. UV light from a high-pressure mercury lamp (USHIO UM-452) was irradiated to the vertically placed glass plates with the zeolite sample at room temperature. The glass plates were reversed after 2 h and the irradiation was continued for another 2 h. The total irradiation time was 4 h (both sides respectively for 2 h). The UV-irradiated sample thus obtained was left at rest for 12 h at room temperature or at 80 °C to promote the reaction of the grafted benzene moiety with an acid molecule formed by the photo-irradiation. The resulting powder was washed with various kinds of solvents (dichloromethane, methanol and THF) for removing unreacted PAG and other by-products, and finally dried at 60 °C for 12 h.

2.3. Analyses

The catalytic reaction of α-methyl styrene dimerization used for estimating the pore situation in our previous paper [27] was not attempted, because we wished to focus on the control of the permeation of molecular nitrogen in this research. The pore closure situations of a variety of zeolites were analyzed only by nitrogen adsorption characteristics. The nitrogen adsorption–desorption isotherms were obtained at −196 °C (in liquid N_2) using a Bellsorp Mini instrument (BEL JAPAN, Inc.). The specific surface areas and the pore volumes of samples were calculated using BET plot and MP method with their adsorption branches of the isotherms, respectively. In all figures of nitrogen sorption isotherms, the corresponding desorption branches were omitted for clear indication due to nearly complete overlaps with adsorption branches. Powder X-ray diffraction patterns were recorded using Mac Science MXP3V diffraction meter with Ni filtered Cu Kα radiation. Diffuse reflectance UV spectra were obtained with a JASCO V-550 spectrometer equipped with an integrating sphere. Kubelka–Munk functions were plotted against the wavelength. UV spectra of solutions were measured using JASCO V-530 spectrometer.

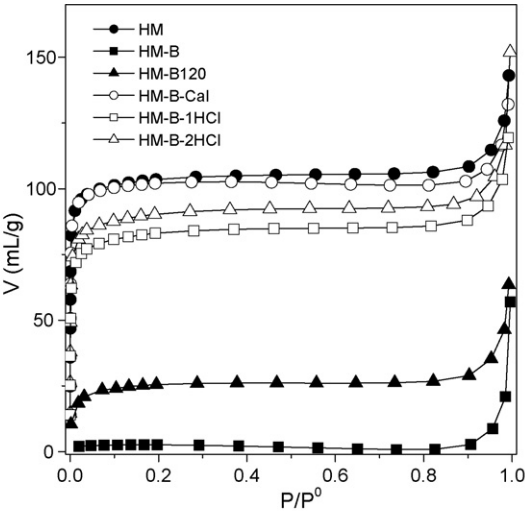

Fig. 2. Nitrogen adsorption isotherms of proton type mordenite (HM) samples in various pore situations using benzene-1,4-diboronic acid. HM (original mordenite), HM-B (grafted at 150 °C), HM-B120 (grafted at 120 °C), HM-B-Cal (calcined HM-B), HM-B-1HCl (1 M HCl treated HM-B), and HM-B-2HCl (2 M HCl treated HM-B).

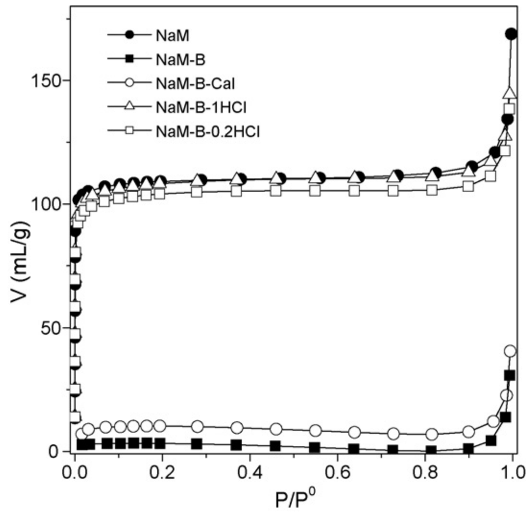

Fig. 3. Nitrogen adsorption isotherms of sodium type mordenite (NaM) samples in various pore situations using benzene-1,4-diboronic acid. NaM (original mordenite), NaM-B (grafted at 150 °C), NaM-B-Cal (calcined NaM-B), NaM-B-1HCl (1 M HCl treated NaM-B), and HM-B-0.2HCl (0.2 M HCl treated NaM-B).

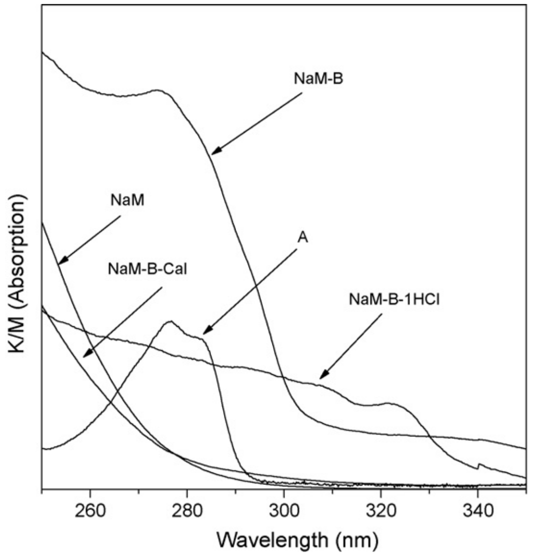

Fig. 4. Diffuse reflection UV spectra of various sodium type mordenite. NaM (original mordenite), NaM-B (grafted), NaM-B-Cal (calcined NaM-B), NaM-B-1HCl (HCl treated NaM-B), and benzene-1,4-diboronic acid (**A**) in acetonitrile (absorption spectrum).

3. Results and discussion

3.1. Sealing and reopening of mordenite micropore using benzene-1,4-diboronic acid

In this study, we selected mordenite and ZSM-5 type zeolites for pore sealing and reopening experiments as well as our previous research [27]. The pore closure using disilylbenzene compounds such as compound **B** were perfectly achieved in the cases of mordenite and ZSM-5. However, the pore closures of zeolite beta and Y-type zeolite were incomplete in our experiments probably due to their wider micropores. The results of pore closures of zeolite beta and Y-type zeolite are shown in the reference [28]. The molecular size of benzene-1,4-diboronic acid (**A**) is less bulky than 1,4-bis(hydroxydimethylsilyl)benzene (**B**) mainly because of the absence of four methyl groups. As the effective sealing of the micropores of zeolite beta and Y-type zeolite will not be expected by using benzene-1,4-diboronic acid, we did not utilize those zeolites in this research.

Figs. 2 and 3 show the nitrogen adsorption isotherms of proton type and sodium type mordenite samples in various pore situations, respectively. The specific surface areas by BET method and the pore volumes by MP method estimated from the isotherms are summarized in Table 1. The grafting temperature at 120 °C was not effective for the perfect sealing of the micropore in the case of the diboronic acid (HM-B120). Nitrogen adsorbed to this sample considerably as shown in Table 1 and Fig. 2, although the grafting treatment at this temperature completely restricted the adsorption of nitrogen in the case of disilylbenzene compounds [27]. Perfect pore sealing was succeeded by the grafting process at higher temperature (150 °C) as shown in Fig. 2 (HM-B). The specific surface area and the pore volume were reduced to 10 m^2/g or less than 0.001 mL/g, respectively (Table 1). The calcination of this modified sample at 500 °C for 6 h revived the porosity of the mordenite totally (HM-B-Cal). This full recovery was also observed in the case of disilylbenzene compounds. The reopening of the micropores was also achieved by HCl treatment even at room temperature. No heating that is essential for disilylbenzene compounds [27] was required in this case. Approximately 85% of pore volume was recovered by using 2 M HCl solution. Even in the 1 M solution of HCl, high pore reopening (about 78% recovery) was achieved. Thus, the pore reopening process with HCl solution proceeded under milder conditions than disilylbenzene compounds.

The micropore of sodium type mordenite was successfully sealed by benzene-1,4-diboronic acid as well as proton type one. By grafting at 150 °C, the specific surface area and the pore volume decreased to 13 m^2/g or <0.001 mL/g, respectively (NaM-B). The presence of benzene-1,4-diboronic acid moiety was ascertained by the characteristic UV absorption of benzene group around 270–280 nm as shown in Fig. 4. When this boron-modified sodium

Table 1
Porosity properties of mordenite zeolite with various modifications.

Sample name	Modification	Specific surface area (m^2/g)[a]	Pore volume (mL/g)[b]
HM	–	401	0.172
HM-B120	Grafted at 120 °C	92	0.039
HM-B	Grafted at 150 °C	10	<0.001
HM-B-Cal	Calcined at 500 °C	407	0.163
HM-B-1HCl	Treated with 1 M HCl at rt	319	0.134
HM-B-2HCl	Treated with 2 M HCl at rt	348	0.146
NaM	–	417	0.180
NaM-B	Grafted at 150 °C	13	<0.001
NaM-B-Cal	Calcined at 500 °C	38	0.010
NaM-B-1HCl	Treated with 1 M HCl at rt	421	0.182
NaM-B-0.2HCl	Treated with 0.2 M HCl at rt	406	0.173

[a] BET specific surface area.
[b] MP pore volume.

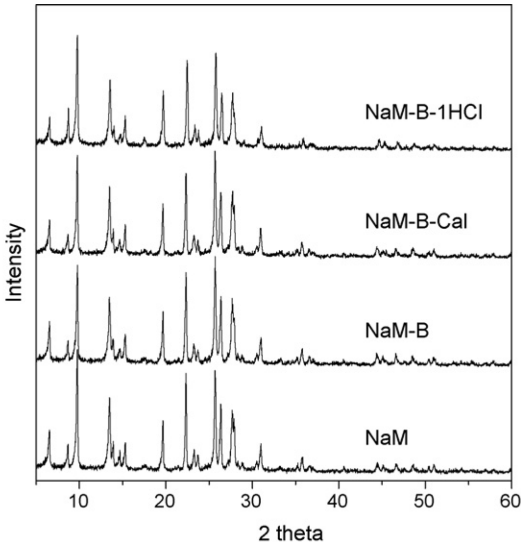

Fig. 5. Power X-ray diffraction patterns of various sodium type mordenite; NaM (original mordenite), NaM-B (grafted), NaM-B-Cal (calcined NaM-B), NaM-B-1HCl (HCl treated NaM-B).

type mordenite (NaM-B) was calcined at 500 °C, the pore properties were not recovered (NaM-B-Cal). Only 5% of pore volume was revived in this calcined sample, while the perfect recovery of the pore property was found in the proton type mordenite (HM-B-Cal). The complete disappearance of the UV absorption around 280 nm in the calcined sample (NaM-B-Cal) indicated the successful removal of the benzene moiety by this calcination treatment. In addition, no significant differences of the crystalline structures were observed among all mordenite samples after various modification-treatment processes according to the XRD patterns summarized in Fig. 5. It is clear that no collapse of the microporous structure of the mordenite occurred in the calcined sample (NaM-B-Cal). Thus, neither the residual benzene moiety nor the disruption of the crystalline structure of mordenite was responsible for the little recovery of the porosity of sodium type mordenite after calcination. It is well known that the loading of boron atom into zeolite materials create cation exchange sites [29,30]. The sodium cations in sodium type mordenite that were not removed by calcination might interact with the negatively charged sites of boron as shown in Fig. 6. These two metal cations occluded the micropore of zeolite to result in no adsorption of nitrogen in the calcined sample (NaM-B-Cal).

On the other hand, HCl treatment was very effective for reopening the micropore. The perfect recovery of the pore volume was found even in the treatment of 0.2 M HCl solution at room temperature (NaM-B-0.2HCl). The disappearance of UV absorption around 280 nm was ensured in the sample NaM-B-1HCl as shown in Fig. 4. The treatment of HCl cleaved the boron-carbons in benzene-1,4-diboronic acid moiety. Even in this case, boron atom is likely to remain in the zeolite powder. Although the dealumination of mordenite by the acid treatment is naturally concerned, our current conditions of HCl treatment were milder than our previous paper [27]. It is thought that no significant aluminium leaching might occur under these conditions. However, the cation exchange between sodium cation and acidic proton took place to avoid the blockage effect of sodium cation observed in the calcination treatment. Finally, the complete recovery of the pore volume was achieved in the treatment of HCl solutions.

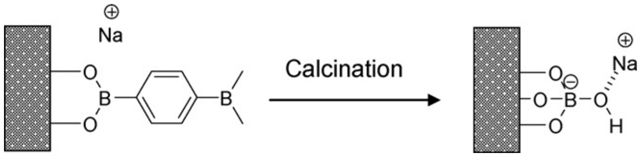

Fig. 6. A plausible mechanism of pore blockage after calcination in the case of sodium type zeolites.

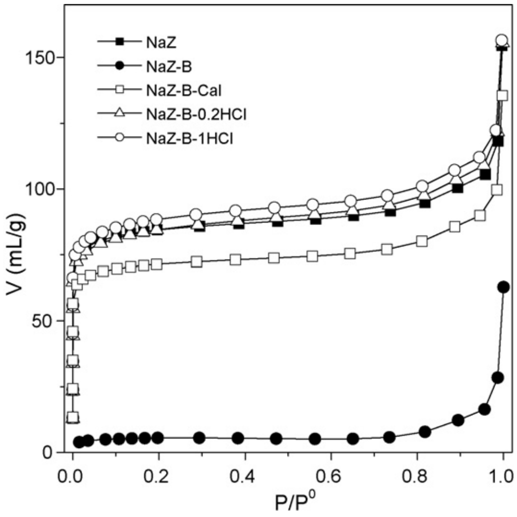

Fig. 7. Nitrogen adsorption isotherms of sodium type ZSM-5 (NaZ) samples in various pore situations. NaZ (original Na-ZSM-5), NaZ-B (grafted), NaZ-B-Cal (calcined NaZ-B), NaZ-B-1HCl (1 M HCl treated NaZ-B), and HZ-B-0.2HCl (0.2 M HCl treated NaZ-B).

3.2. Sealing and reopening of ZSM-5 micropore using benzene-1,4-diboronic acid

Next, we examined the pore sealing and the reopening using ZSM-5 type zeolite. At first, benzene-1,4-diboronic acid was grafted onto a proton type ZSM-5 (H-ZSM-5: $SiO_2/Al_2O_3 = 39$) under the similar conditions to the proton type mordenite (HM-B). This sample turned dark brown after the grafting process, although no blackening was found in the case of the proton type mordenite. This dark brown color completely disappeared by the calcination at 500 °C, and the nitrogen adsorption property was recovered. These observations suggested the coke formation occurred. Therefore, the high acidity of H-ZSM-5 might produce coke component from benzene-1,4-diboronic acid to blacken the zeolite sample. Then, a sodium type ZSM-5 (Na-ZSM-5: $SiO_2/Al_2O_3 = 23.8$) was employed for the grafting. In this case, no color change of the zeolite sample was observed. Therefore, only the sodium type ZSM-5 was used for the further experiments of the pore sealing and the reopening. Fig. 7 shows the nitrogen adsorption isotherms of Na-ZSM-5 samples in various pore situations. The corresponding specific surface areas and the pore volumes of samples are listed in Table 2. The sealing of the micropore was successfully achieved, and the pore volume was reduced to less than 0.001 mL/g (NaZ-B). Although the nitrogen adsorption of the calcined sample (NaZ-B-Cal) did not return to that of the original Na-ZSM-5, approximately 70% of pore volume was regenerated. According to the size comparison between the micropores of zeolites (mordenite and ZSM-5) and benzene-1,4-diboronic acid, it is thought that this boronic acid can considerably penetrate into the pore of mordenite. On the other hand, the micropore of ZSM-5 is narrower than that of mordenite and the penetration of the boronic acid must be suppressed considerably. The molecular size of benzene-1,4-diboronic acid was estimated with Chem 3D modeling, and the distance between different boron atoms is approximately 0.6 nm, that is large enough to the pore of ZSM-5 (pore size: 0.56 nm × 0.53 nm and 0.55 nm × 0.51 nm). Benzene-1,4-diboronic moiety seems to be located predominately on the

Table 2
Porosity properties of ZSM-5 type zeolite with various modifications.

Sample name	Modification	Specific surface area (m^2/g)[a]	Pore volume (mL/g)[b]
NaZ	–	328	0.126
NaZ-B	Grafted at 150 °C	20	<0.001
NaZ-B-1HCl	Treated with 1 M HCl at rt	337	0.126
NaZ-B-0.2HCl	Treated with 0.2 M HCl at rt	316	0.125
NaZ-B-Cal	Calcined at 500 °C	249	0.090
NaZ-B-PAG	UV irradiation with PAG[c]	229	0.086
NaZ-B-UV	UV irradiation[c]	166	0.050
NaZ-Si	Grafted at 120 °C	21	<0.001
NaZ-Si-PAG1	UV irradiation with PAG[c]	28	0.004
NaZ-Si-PAG2	UV irradiation with PAG[d]	79	0.021

[a] BET specific surface area.

[b] MP pore volume.

[c] Left at room temperature after UV irradiation and washed.

[d] Left at 80 °C and washed.

exterior surface of ZSM-5. The sodium migration apparently occurring in the micropore of mordenite (Fig. 6) took place preferentially on the exterior surface of ZSM-5. Therefore, the recovery of the micropore of ZSM-5 was significantly achieved by calcination (70%).

On the other hand, HCl treatment at room temperature completely revived both the specific surface area and the pore volume (NaZ-B-1HCl and NaZ-B-0.2HCl). A diluted solution (0.2 M HCl) was equally effective to 1 M HCl solution. This is probably because the benzene-1,4-diboronic moiety placed on the exterior surface was sensitive to the reaction with HCl. Furthermore, the cation exchange took place between sodium cation and acidic proton as well as sodium type mordenite. Eventually, the complete reopening of the micropore was achieved successfully.

3.3. *Reopening of zeolite micropores using photo-acid generators (PAG)*

As mentioned above, acidic treatment was ascertained to be effective for removing the grafted benzene moiety and reopening the micropore sealed by it. However, this process carried out in solution system requires some troublesome procedures such as filtration and drying. Solid phase processes of the reopening of the micropore will provide more sophisticated systems for manipulating the micropores of zeolitic materials. Recently, a photo-induced acid generation in solid phase is actively studied. Especially, photo-acid generators (PAG) supply some interesting technologies of acidic reactions [31–33]. Naphthalimide trifluoromethanesulfonate (compound **C** in Fig. 1) as PAG generates a strong acid species (trifluoromethanesulfonic acid) by UV irradiation [34–36]. This is advantageous to reopen the micropore of zeolites in solid phase. Moreover, this process provides an advanced technique that only the micropores of the domains exposed to the UV light can be reopened, which is expected to be utilized in nano manipulations of gaseous small molecules. Here, we attempted to establish fundamental techniques for creating the reopening process of micropores by UV irradiation in solid phase.

A dichloromethane solution of *N*-hydroxynaphthalimide trifluoromethanesulfonate was impregnated to boronic acid-modified ZSM-5 (NaZ-B). After the evaporation of solvent, UV light was irradiated to the ZSM-5 solid. Fig. 8 shows the DR-UV spectra of various ZSM-5 samples. The absorption of benzene diboronic moiety around 270–280 nm was weak in the case of ZSM-5 (NaZ-B). In the sample with impregnated PAG, the strong UV absorption of naphthalimide trifluoromethanesulfonate was observed at 340 nm. This UV absorption of the PAG gradually decreased with UV irradiation, and finally the adsorption almost disappeared. As shown in Fig. 8, only slight UV absorption was observed after irradiation for 4 h. This solid was kept at room temperature overnight to promote the reac-

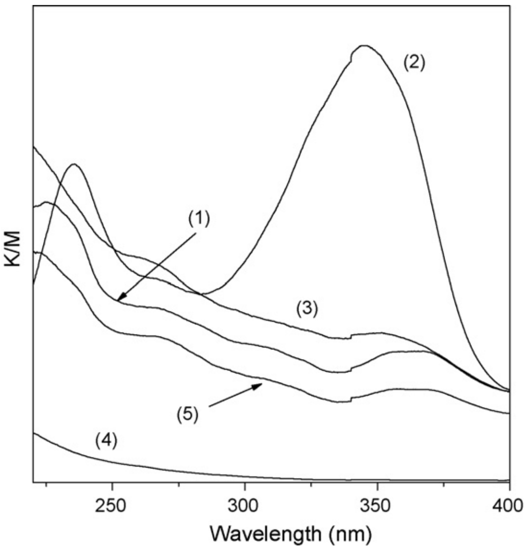

Fig. 8. Diffuse-reflectance UV spectra of Na-ZSM-5 in photo-acid generator processes. (1) NaZ-B, (2) NaZ-B with impregnated PAG before UV irradiation, (3) NaZ-B with impregnated PAG after UV irradiation before washing, (4) NaZ-B with impregnated PAG after UV irradiation and washing (NaZ-B-PAG), (5) NaZ-B-UV.

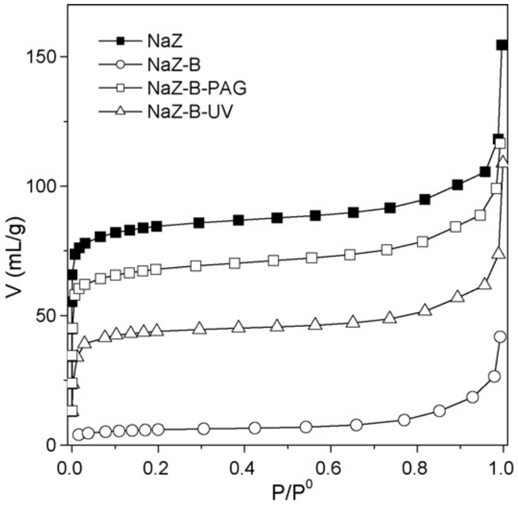

Fig. 9. Nitrogen adsorption isotherms of sodium type ZSM-5 (NaZ) samples modified with benzene-1,4-diboronic acid in various pore situations. NaZ (original Na-ZSM-5), NaZ-B (grafted), NaZ-B-PAG (NaZ-B with impregnated PAG after UV irradiation and washing), NaZ-B-UV (NaZ-B without impregnated PAG after UV irradiation and washing).

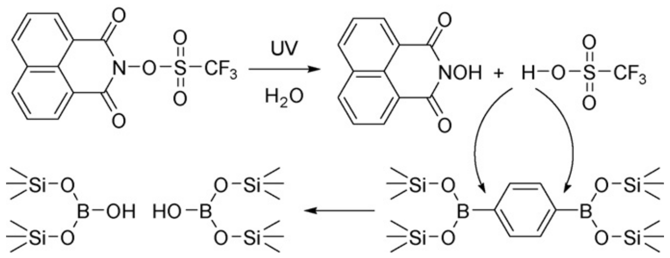

Fig. 10. Reopening of micropore of zeolite by photo-acid generator with UV irradiation.

tion of trifluoromethanesulfonic acid (formed from the PAG) with benzene diboronic moiety. The resulting powder was washed with various kinds of solvents for removing unreacted PAG and other by-products. At this stage, no clear UV absorption was observed in the solid to show the successful removal of the benzene diboronic moiety and other by-products.

The nitrogen adsorption isotherms of these zeolite samples are shown in Fig. 9. The corresponding porosity data are listed in Table 2. Approximately 70% of MP pore volume was regenerated by this PAG treatment in solid phase (NaZ-B-PAG). It is thought that this regeneration of micropore of Na-ZSM-5 was caused from the acidic cleavage of carbon–boron bonds with the acid species formed by UV irradiation as shown in Fig. 10. No perfect regeneration of the pore property is thought to result from the effect of the remained sodium cation in the resulting sample, because no dissolution process of sodium cation was involved. UV irradiation without impregnated PAG to NaZ-B was also examined as a control experiment. After the irradiation of UV light for 4 h, the powder was washed in the similar manners to NaZ-B-PAG. The DR-UV spectrum of this sample is also indicated in Fig. 8. Although a moderate regeneration of the micropore was found even in this case as shown in Fig. 9 and Table 2, the absorption around 270–280 nm was still found in this spectrum to indicate the remaining of the benzene diboronic moiety. The recovery of approximately 40% of MP pore volume was less than UV irradiation with the impregnated PAG. UV irradiation without PAG was found to be considerably effective for the pore reopening. This process is also an expected treatment because of its simpler procedures. As the photo cleavage process of silicon–carbon bond is common recently [37], this process will promote new boron chemistry with light irradiation.

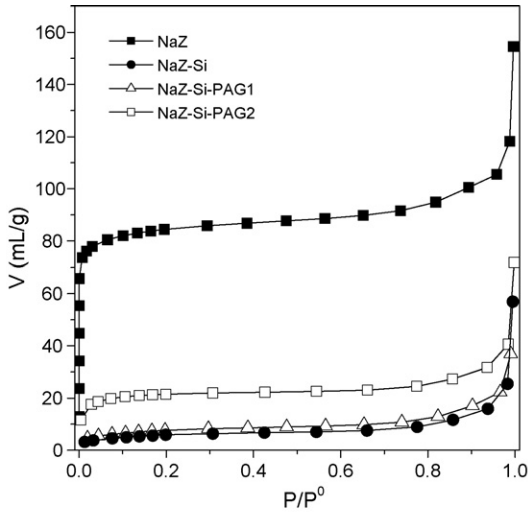

Fig. 11. Nitrogen adsorption isotherms of sodium type ZSM-5 (NaZ) samples modified with 1,4-bis(hydroxydimethylsilyl)benzene (**B**) in various pore situations. NaZ (original Na-ZSM-5), NaZ-Si (grafted), NaZ-Si-PAG1 (left at rt), NaZ-Si-PAG2 (left at 80 °C).

We also attempted this pore reopening process using the PAG to the Na-ZSM-5 modified with 1,4-bis(hydroxydimethylsilyl)benzene. In the first experiment, after PAG impregnation and the following UV irradiation, this sample was left at room temperature as well as the case of benzene-1,4-diboronic acid. The porosity properties of this sample (NaZ-Si-PAG1) did not change as indicated in Fig. 11 and Table 2. The still standing treatment of the UV irradiated sample at 80 °C moderately regenerated the porosity (NaZ-Si-PAG2). In our previous report using disilylbenzene compound [27], the HCl treatment at room temperature was not effective for reopening the micropore, while heating treatment at 80 °C achieved the regeneration of micropores of zeolite samples. Even in the case of UV irradiation with PAG in solid phase, the heating process was necessary to the reopening of the micropore. These results also revealed that benzene-1,4-diboronic acid is far superior to 1,4-bis(hydroxydimethylsilyl)benzene for the reopening of zeolite micropores under milder conditions.

4. Conclusions

We showed here that the micropores of mordenite and ZSM-5 zeolites were completely sealed with benzene-1,4-diboronic acid as well as 1,4-bis(dimethylsilyl)benzene derivatives reported in our previous paper [27]. Molecular nitrogen cannot permeate into the micropore thus closed. The reopening of the sealed micropores was achieved by calcination or HCl treatment under milder conditions (at room temperature) than 1,4-bis(dimethylsilyl)benzene derivatives. In some cases, the sealed micropores were completely reopened by the HCl treatment at room temperature. The reopening of the micropores was also accomplished by the UV irradiation to the solid zeolites with an impregnated photo-acid generator (PAG). PAG compounds are actively employed in photo-resist, micropatterning and other light-related technologies. The pore reopening of the micropores with photo-irradiation in solid phase will be useful for the photo-responsive gas separation and related processes, because photo-irradiation can be manipulated freely in terms of time and space.

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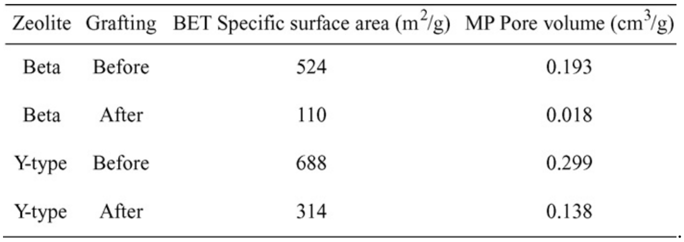
[28] The porosity properties of zeolite beta and Y-type zeolite before and after grafting 1,4-bis(hydroxydimethylsilyl)benzene (**B**) are summarized in the following table.



Zeolite	Grafting	BET Specific surface area (m^2/g)	MP Pore volume (cm^3/g)
Beta	Before	524	0.193
Beta	After	110	0.018
Y-type	Before	688	0.299
Y-type	After	314	0.138

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