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ORIGINAL CONTRIBUTION

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Reactivity of silanol groups on zeolite surfaces

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Abstract Alkyl group introduction into zeolite surfaces was attempted utilizing the reactivity of surface silanol groups as lattice defects resulting from hydrothermal or acid treatment of zeolites. The reaction was carried out using organosilane and alcohols, and traced by in situ IR measurement as well as by elemental analysis. In situ IR measurement demonstrated high reactivity of terminal silanol groups. A good correlation was noted between the amount of reacted groups and the amount of terminal silanol groups, indicating high reactivity of terminal silanol groups and very low reactivity of silanol groups that form hydroxy nests. Treated zeolite exhibited high hydrophobicity, such that it floats on water.

Key words Modification – faujasite – surface silanol groups – hydroxy nests – alkyl group introduction

Introduction

Surface functional groups, such as silica gel [1–8], silica [9–14] and zeolite [15] surface silanol groups, are known to possess relatively high chemical reactivity; on the basis of this reactivity, various surface-improving agents have been used to modify surface characteristics. The present authors determined the densities of two kinds of silanol groups resulting from hydrothermal and acid treatments of faujasite zeolites, and revealed several differences in their properties [16].

With this in mind, we examined the reactivities of two kinds of silanol groups with organosilane and various alcohols, with the aim of enhancing the hydrophobicity of essentially hydrophilic zeolite surfaces by alkyl group introduction.

In order to assess the reactivities of surface silanol groups resulting from hydrothermal and acid treatments, their reactivities with dimethoxydimethylsilane (DMDMS) were estimated from in situ IR measurements. Also examined were the reactivities with various alcohols of different types and lengths of carbon chain, and methoxytrimethylsilane (MTMS) which has a single reactive group, via in situ IR measurement and elemental analysis. Pore structural changes found in treated samples were analyzed by the *t*-plot method [17, 18], on the basis of nitrogen adsorption measurements. Hydrophilic–hydrophobic characteristics were assessed from water adsorption and dispersibility in water as well as in *n*-heptane.

Experimental

Zeolites used in this study are shown in Table 1 and described in detail elsewhere [16]. Organosilanes used were purified by the freeze–pump–thaw cycle method. Alcohols were dehydrated with a molecular sieve 4A.

DMDMS treatment was performed in liquid (cyclohexane solution) and gas phases. Liquid-phase treatment was performed as follows: About 10 g of zeolites was

Table 1 Chemical compositions of the samples determined by chemical analysis

	SiO_2	Al_2O_3	Na_2O	SiO_2/Al_2O_3
	[wt%]			
Na-$Y_{5.5}$	67.1	20.6	12.5	5.5
H-Y_{14}	89.5	10.5	0.02	14.5
H-Y_{40}	95.6	4.0	0.03	40.4
H-Y_{144}	98.8	1.16	<0.05	144
H-Y_{770}	99.8	0.22	<0.01	770

These values were determined by Tosoh Corp.

Table 2 DMDMS treatment conditions

		DMDMS amount
H-Y_{770}D	Liq. phase	10 ml
H-Y_{770}D2	Liq. phase	50 ml
H-Y_{770}DV2	Gas phase	—

treated at 673 K under 1 mPa for 5 h, to which cyclohexane, dehydrated with a molecular sieve 4A, was added until the zeolite was thoroughly immersed. After the mixture was transferred to a 1000 ml three-mouthed separable flask, cyclohexane was added to a total volume of about 500 ml and 10 ml of DMDMS was added, followed by 24 h of reaction with refluxing and stirring at 353 K. The reaction mixture was then cooled to room temperature, filtered, and washed with cyclohexane several times, after which the filtrate was dried under vacuum at room temperature.

Gas-phase treatment was performed as follows: About 5 g of H-Y_{770} previously treated at 673 K under 1 mPa for 5 h, was subjected to contact with vaporized DMDMS at for 36 h. Since the contact reaction gives forth CH_3OH as a by-product, resulting in an increase of up to several kPa in reaction system pressure, the sample was degassed several times during the reaction to remove CH_3OH. After completion of the reaction, the sample was dried under vacuum at room temperature.

The detailed treatment conditions for the samples are shown in Table 2.

Esterification using various alcohols was performed as follows: After pretreatment at 423 K under 1 mPa for 5 h, about 5 g of H-Y_{770} was brought into contact with about 100 ml of each alcohol, without atmospheric contact, at room temperature in a sealed vessel. The reaction was carried out under the conditions shown in Table 3, while the mixture was stirred using an autoclave for methanol and ethanol, each having a relatively low boiling point, or by refluxing at the respective boiling points for *n*-butanol, *n*-hexanol and benzyl alcohol. After completion of the treatment, each sample was filtered, followed by thermal evacuation under the conditions shown in Table 3, to remove all unreacted alcohol.

The treatment of H-Y_{770} with MTMS was performed in gas phase, and its procedure was similar to that with DMDMS and shown in Table 3.

The amount of silanol groups of H-Y_{770} was determined by the reaction with thionyl chloride in the similar procedure to the literature by Boehm [19] and is reported in detail elsewhere [16].

In situ IR measurements were carried out as follows: Each sample, about 10.0 mg was pressed with a dice 13 mm in diameter at 49 MPa to yield a sample wafer, which was placed in an in situ cell of quartz with a NaCl window, and analyzed using a JASCO IR-810 infrared spectrophotometer (wave number accuracy = $\pm 2\ cm^{-1}$, resolution = $2.7\ cm^{-1}$ at $1000\ cm^{-1}$). The wavelength was corrected using polystyrene film.

Water adsorption isotherms were determined on the basis of gravimetric measurements at 298 K using a quartz spring and charge coupled device (CCD) for position detection. The water used was purified by the freeze–pump–thaw cycle method.

Nitrogen adsorption was measured at liquid nitrogen temperature using a volumetric adsorption apparatus. Each sample, about 200 mg, was weighed out in a sample tube and pretreated at 673 K under 1 mPa for 5 h.

Table 3 Esterification or silanization and post-treatment conditions

			Esterification or silanization	Evacuation
H-Y_{770}MeOH	Methanol	Autoclave	408 K, 0.91 MPa, 24 h	423 K, 12 h
H-Y_{770}EtOH	Ethanol	Autoclave	423 K, 0.91 MPa, 24 h	423 K, 12 h
H-Y_{770}BuOH	1-Butanol	Reflux	391 K, 24 h	403 K, 12 h
H-Y_{770}HxOH	1-Hexanol	Reflux	431 K, 24 h	423 K, 12 h
H-Y_{770}BzOH	Benzyl alcohol	Reflux	478 K, 24 h	473 K, 12 h
H-Y_{770}MTMS	Methoxytrimethylsilane	Gas phase	673 K, 24 h	673 K, 12 h

Elemental analysis was performed using a MT-3 analyzer (Yanako Bunseki Kogyo), with 2 mg of antipyrine ($C_{11}H_{12}ON_2$) as a reference.

Results and discussion

Figure 1 shows the temperature dependence of gas-phase reaction of H-Y_{770} with DMDMS as determined by the in situ IR measurement. The reaction was performed in an IR cell at various temperatures, and the spectra were taken at room temperature after the unreacted DMDMS was evacuated. As the temperature increased, the band having an absorption peak at 3730 cm^{-1}, assigned to the terminal silanol group, decreased its absorbance, while another absorption band appeared at 3000–2800 cm^{-1}, assigned to alkyl group C–H stretching vibration, suggesting an irreversible reaction of DMDMS with the terminal silanol group. At higher temperature the absorption band at 3730 cm^{-1} almost disappeared which indicates that almost all terminal silanol groups reacted. By contrast, the band at 3700–3000 cm^{-1}, assigned to hydroxy nests [16], showed no significant change, which suggests that the hydroxy nests are not significantly involved in the reaction with DMDMS. These findings demonstrate that DMDMS reacts preferentially with the terminal silanol group in DMDMS treatment. Since all terminal silanol groups disappeared at 673 K, this temperature appears to be appropriate for DMDMS treatment in a gas phase. The band intensity of hydroxy nests decreased to some extent at 673 K, which might be due to their dehydration–condensation since the band intensity of alkyl groups remained unchanged compared to that at 573 K. Since the hydroxy nests were found not to interact even with water because of the formation of closed hydrogen bond as well as siloxane bond among them [16, 20], their reactivity with organosilanes should be limited.

Figure 2 shows the IR spectra of original H-Y_{770} and DMDMS-treated ones, H-Y_{770}D and H-Y_{770}DV2, which were pretreated at 673 K under 1 mPa. H-Y_{770}DV2, prepared by treating H-Y_{770} in a gas phase, yielded almost the same spectrum as those in Fig. 1. H-Y_{770}D was prepared by treating H-Y_{770} with 10 ml of DMDMS in a liquid phase. A residual band at 3730 cm^{-1} suggests a lack in the amount of DMDMS used. In fact, the spectrum (not shown) of H-Y_{770}D2, prepared by treating H-Y_{770} with 50 ml of DMDMS in a liquid phase, was almost the same with that of H-Y_{770}DV2.

The above IR measurements demonstrate that the terminal silanol group and DMDMS react with each other in both liquid and gas phases.

Figure 3 shows the isotherms of water adsorption at 298 K on untreated (H-Y_{770}) and treated (H-Y_{770}D, H-Y_{770}DV2) samples. The isotherm for H-Y_{770} was of type IV in the BDDT classification, suggesting low affinity for water and supporting the hydrophobic character of H-Y_{770} demonstrated by measurements of immersional

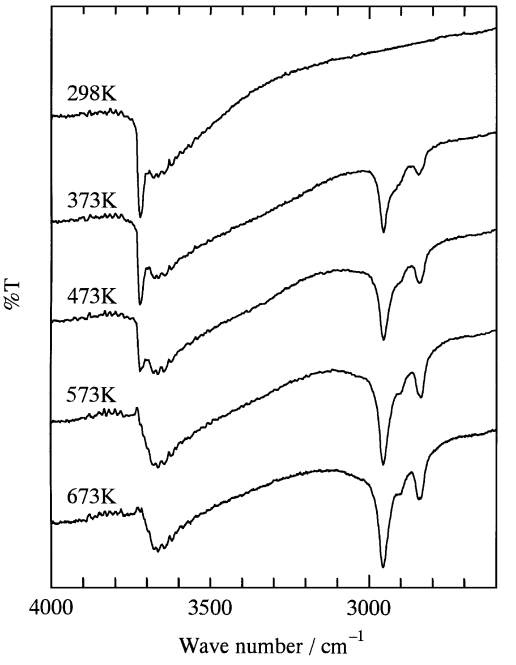

Fig. 1 Temperature dependence of gas-phase reactioin of H-Y_{770} with DMDMS as determined by in situ IR measurement

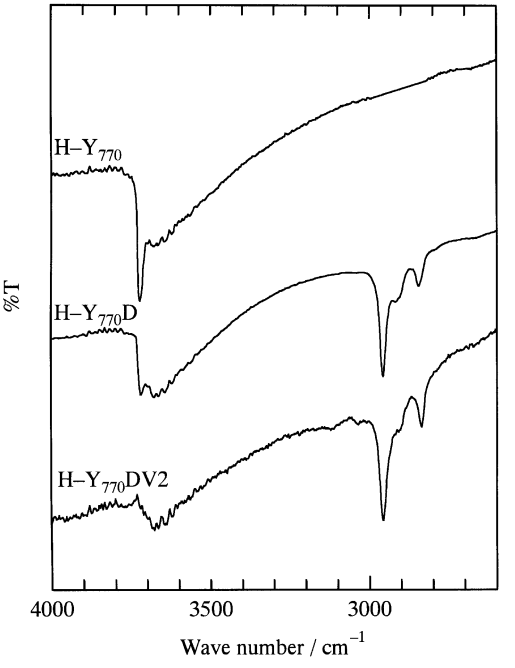

Fig. 2 IR spectra of original H-Y_{770} and DMDMS-treated ones

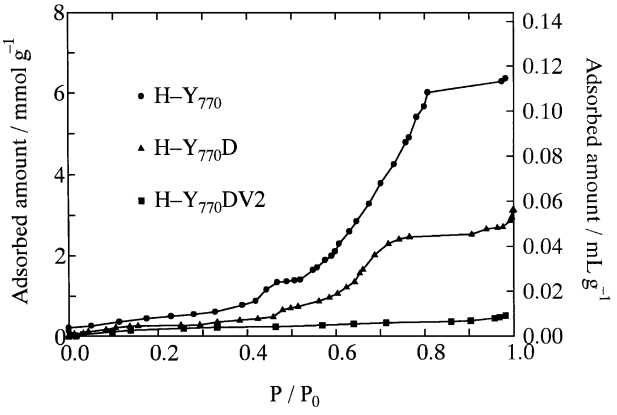

Fig. 3 Isotherms of water adsorption at 298 K on original H-Y$_{770}$ and DMDMS-treated ones

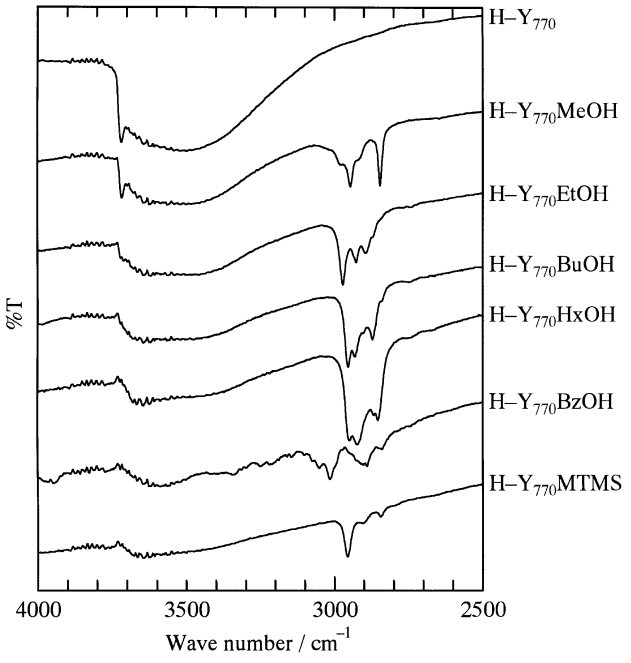

Fig. 4 In situ IR spectra of samples before and after treatments with various alcohols and MTMS

heats in water [20]. After DMDMS treatment, adsorption amount decreased drastically and depended on the degree of the treatment. These facts indicate that DMDMS treatment is effective in making the zeolite surface more hydrophobic.

Figure 4 shows the in situ IR spectra of samples before and after the treatment with various alcohols and MTMS. All treatments resulted in a decrease in the absorbance of the absorption band at 3730 cm^{-1}, assigned to the terminal silanol group, and the appearance of another absorption band at 3000–2800 cm^{-1}, assigned to C–H stretching vibration. These results suggest that esterification or silanization occurred between the terminal silanol group on the zeolite surface and each alcohol or silane, resulting in alkyl group introduction into the zeolite surface. In methanol-treated H-Y$_{770}$ (H-Y$_{770}$MeOH), about half the terminal silanol groups remained unreacted. A small number of unreacted terminal silanol groups were also noted in ethanol-treated H-Y$_{770}$ (H-Y$_{770}$EtOH). In *n*-butanol-treated H-Y$_{770}$ (H-Y$_{770}$BuOH), *n*-hexanol-treated H-Y$_{770}$ (H-Y$_{770}$HxOH), benzyl alcohol-treated H-Y$_{770}$ (H-Y$_{770}$BzOH) and methoxytrimethylsilane-treated H-Y$_{770}$ (H-Y$_{770}$MTMS), no absorption band appeared at 3730 cm^{-1}. The C–H absorption band intensity increased with the increase in carbon chain length of the alcohol used in the reaction. For all treated samples, alkyl group introduction into the zeolite crystal particle surface resulted in a considerably diminished cohesive force among particles.

Table 4 shows the elemental analysis results for samples before and after the treatment. Treated samples were found to contain carbon; in the *n*-alcohol-treated sample, the carbon content increased with the number of carbon chains. By use of the outer surface area and secondary pore surface area of H-Y$_{770}$ [16], alkyl group density could be calculated as about 3 groups nm^{-2} for H-Y$_{770}$BuOH, H-Y$_{770}$HxOH and H-Y$_{770}$MTMS, showing fair agreement with the surface silanol group density of H-Y$_{770}$ calculated by the thionyl chloride method, though the former was about 25% higher than the latter. The surface silanol group density determined by thionyl chloride was found to coincide with that of the terminal silanol groups calculated from IR spectra [16].

Table 4 Elemental analysis results for samples before and after the treatment

	Carbon	Weight loss	Func. groups
	[wt%]	[wt%]	[Groups nm^{-2}]
H-Y$_{770}$	<0.01	5.05	2.4[a)]
H-Y$_{770}$MeOH	1.06	2.16	4.1
H-Y$_{770}$EtOH	2.05	2.93	4.0
H-Y$_{770}$BuOH	2.98	3.90	3.0
H-Y$_{770}$HxOH	4.60	7.52	3.1
H-Y$_{770}$BzOH	15.9	16.5	10
H-Y$_{770}$MTMS	2.38	1.69	3.1
H-Y$_{14}$BuOH	0.96	—	2.1
H-Y$_{40}$BuOH	1.66	—	3.4
H-Y$_{144}$BuOH	2.05	—	2.7

[a)] By $SOCl_2$ method.

From the IR spectral measurements for H-Y$_{770}$BuOH, H-Y$_{770}$HxOH and H-Y$_{770}$MTMS, it can be concluded that all terminal silanol groups were esterified or silanized. On the other hand, silanol groups forming hydroxy nests

are hardly involved in the esterification or silanization reaction in the BuOH, HxOH and MTMS treatments, since the surface alkyl or silyl group density was similar to the terminal silanol group density, despite the high remaining of hydroxy nests even after the pretreatment at 423 K. As reported in the previous paper [20], immersional heats of zeolites revealed that silanol groups that form hydroxy nests do not affect surface polarity. It can therefore be assumed that the low involvement of such silanol groups in the esterification or silanization reaction is due to their stabilization as a result of mutual binding via hydrogen bonds.

In the case of H-Y_{770}MeOH, IR spectrometry confirmed the remaining of unreacted terminal silanol groups, the surface alkyl group density being 4.1 groups nm^{-2}, exceeding the silanol group density of 2.4 groups nm^{-2}. Similarly, in the case of H-Y_{770}EtOH, the surface alkyl group density of 4.0 groups nm^{-2} exceeded the silanol group density. These results suggest that silanol groups that form hydroxy nests are partly esterified, as are terminal silanol groups, in these areas. Since methanol and ethanol treatments were performed under increased pressure in an autoclave, in view of the low boiling points of methanol and ethanol, the involvement, in the reaction, of silanol groups that form hydroxy nests under increased pressure is suggested.

For H-Y_{770}BzOH, both the carbon content and surface functional group density were extremely high. This finding will be described below, together with nitrogen adsorption measurements.

Figure 5 shows the isotherms for nitrogen adsorption at 77 K for various samples before and after the treatment. Extremely low adsorption was noted in H-Y_{770}BzOH than in other samples. Since benzyl alcohol is known to readily show intermolecular condensation, its condensates remained in zeolite pores without being separated by the procedure for removal of unreacted substances. In H-Y_{770}, the isotherm of type II in the BDDT classification was obtained, due to secondary pore formation following dealumination [16]. However, after *n*-alcohol treatment, the isotherm again approached type I which is typical for regular pore filling. After the treatment, adsorption amount under lower pressure did not increase significantly; this suggests that micropore volume may not be affected in *n*-alcohol treatment.

Figure 6 shows the *t*-plot results for various samples before and after the treatment. After *n*-alcohol treatment, the gradient of the linear portion between 0.2 and 0.7 nm decreased, suggesting secondary pore volume reduction. Table 5 shows the specific surface areas obtained by the BET method, and those calculated from the gradients of the respective linear portions of *t*-plots for different portions (zeolitic micropores, secondary pores, external surfaces) of samples before and after alcohol or organosilane treatment. The unit weight values given in the table are based on zeolitic skeleton weight as calculated from carbon content values obtained from elemental analysis. It is evident that among the specific surface area changes due to alcohol treatment, specific surface areas of secondary

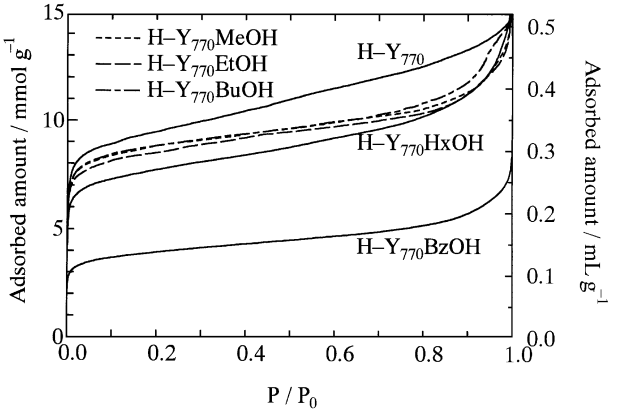

Fig. 5 Isotherms or nitrogen adsorption at 77 K for various samples before and after treatments

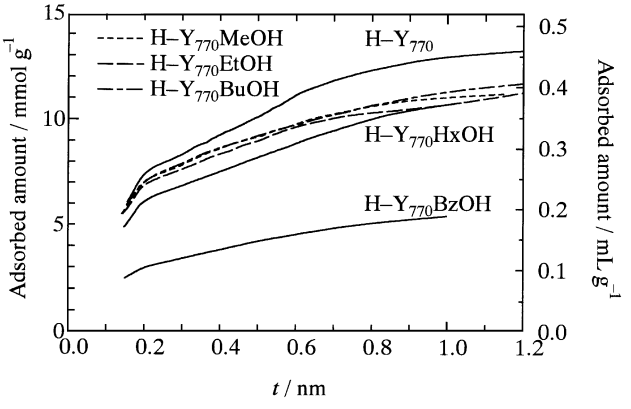

Fig. 6 Results of *t*-plot for various samples before and after treatments

Table 5 Specific surface areas (micropores, secondary pores, external surfaces) of samples before and after alcohol or organosilane treatment

	S_{BET}	Micro.	Sec.	Ext.
	[$m^2 g^{-1}$ dry]			
H-Y_{770}	637	507	108	22.0
H-Y_{770}MeOH	613	507	90.6	15.8
H-Y_{770}EtOH	588	483	75.6	29.7
H-Y_{770}BuOH	615	525	61.0	29.3
H-Y_{770}HxOH	559	443	71.9	43.9

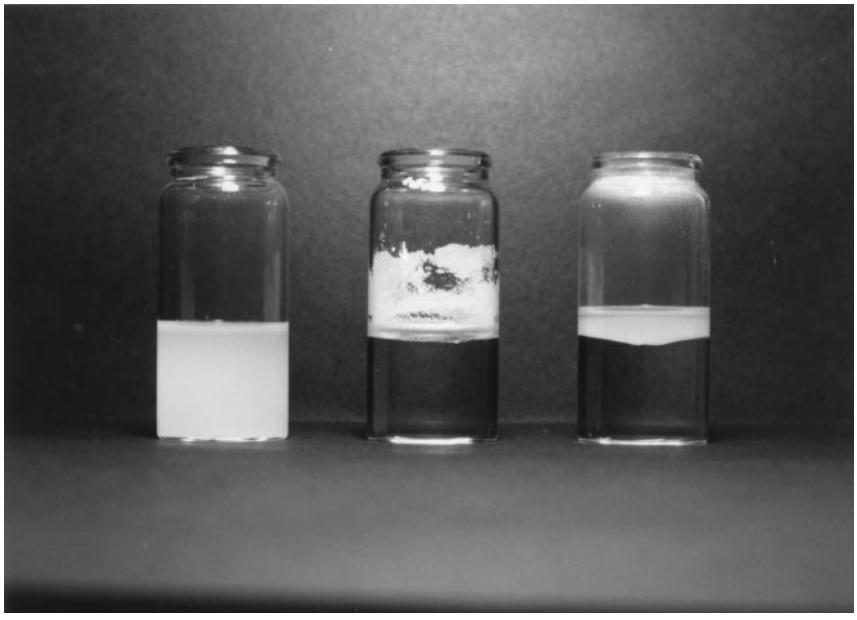

Fig. 7 Dispersibilities of various samples in water and *n*-heptane before and after treatments. Left: H-Y_{770}/H_2O, Center: H-Y_{770} BuOH/H_2O, Right: H-Y_{770}BuOH/*n*-heptane/H_2O

pores decreased markedly. To explain this finding, it can be assumed that alkyl group introduction by *n*-alcohol treatment does not occur on zeolitic micropore surfaces, but on secondary pore and external surfaces, resulting in the secondary pore volume reduction, since terminal silanol groups to be esterified are present on secondary pore surfaces and external surfaces, but not on micropore surfaces.

Figure 7 shows dispersibilities of various samples before and after treatment in water and *n*-heptane. The untreated sample H-Y_{770} showed fairly good dispersibility in water, while H-Y_{770}BuOH had very low dispersibility. The latter separately floated on the water surface, and did not sediment upon stirring, while it showed good dispersibility in *n*-heptane. These results demonstrate that alkyl group introduction into the zeolite surface imparts very high hydrophobicity to zeolite.

Conclusion

Two kinds of silanol groups, resulting from hydrothermal treatment and acid treatment, were found to show different reactivities with organosilanes and alcohols. In situ IR measurements demonstrated that almost all terminal silanol groups irreversibly react with organosilanes and alcohols, the alkyl or silyl group density calculated from carbon content obtained by elemental analysis almost agreeing with the terminal silanol group density. On the other hand, silanol groups that form hydroxy nests undergo almost no reaction with organosilanes or alcohols except the reaction at high pressure and temperature with methanol and ethanol, which may be explained by their mutual binding via hydrogen bonds. For zeolites subjected to hydrothermal or acid treatment, the isotherms for water adsorption were of type IV, suggesting their hydrophobicity; the significant reduction observed in adsorption after DMDMS treatment indicates additional hydrophobicity. Also, alkyl group introduction into the zeolite surface by alcohol treatment provided zeolites with high hydrophobicity, such that they float on water.

These findings suggest that the method of surface modification now in common use for silica and silica gel is also applicable to zeolite.

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