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The appearance of adsorption ability of modified zeolites for sodium dodecylsulfate from its aqueous solution

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Abstract: Hydrophobic faujasite-type zeolites were prepared by the treatment of hydrophilic Na-$Y_{4.6}$ with silicon tetrachloride ($SiCl_4$) by way of dealumination-silicon exchange reaction. Hydrophilic–hydrophobic characters of these zeolite surfaces were evaluated by measurements of immersional heats into water or *n*-hexane. Adsorption rates of sodium dodecylsulfate (SDoS) on these zeolites from its aqueous solution and their adsorption characteristics were investigated, and compared with those on ZSM-5 with various Si/Al ratios.

The adsorption ability of SDoS into zeolite micropores developed on the zeolite only when it was modified to some extent. The adsorption rates of SDoS were very slow and proved to be affected by molecular diffusion in zeolite pores. They depended on hydrophilic-hydrophobic character of zeolites as well as on pore structures. Adsorption isotherms of SDoS were of Langmuir type, which indicates that the adsorption occurred typically into zeolite pores. Adsorbed amount of SDoS depended on the balance of hydrophilic–hydrophobic character and number of cation site of zeolite surfaces, and had a maximum in case of ZSM-5 zeolites.

Key words: Zeolite – modification – surfactant – adsorption

Introduction

Today, many surface active agents (surfactants) are used in industry and households and they induce serious problems of water pollution. Therefore, the removal of such substances should be indispensable prior to water treatments. Adsorption technique is one of the widely used ones, and the application of activated carbon [1–6], activated carbon fiber [7] or clays [8, 9] for the adsorption removal of surfactants or various organics have been reported. In particular activated carbons have already been used in water purification plants and drainages and a number of studies have been reported [10, 11].

Adsorption of organics from their aqueous solution on zeolites has been reported by Narita et al. [12], who investigated adsorption of phenols from aqueous solution on siliceous zeolite, silicalite.

Zeolites are widely used as adsorbents because of their regular pore structure of molecular dimension. However, since they generally contain a number of framework anions (AlO_2^-) and cations, they form a strong electrostatic field on the surface which enhances the ability to adsorb polar molecules such as water by the field-dipole or electrostatic interaction. The significant hydrophilicity of zeolites prevents organic substance to adsorb on them in the presence of water.

ZSM-5 type zeolite with high Si/Al ratio can be synthesized, then their hydrophilic–hydrophobic character can be controlled. However, they have small micropores of 0.55 nm in diameter and small pore volume compared with that of other zeolites, which is disadvantageous for the adsorption of bulky organic substances. On the other hand, the entrance of micropores of faujasite-type zeolites is 0.9 nm in diameter and the interior is 1.3 nm in diameter, which are large enough for the adsorption of bulky substances.

In this study, Na-Y-type zeolites will be modified by $SiCl_4$ treatment in order to replace framework Al by Si atoms. Hydrophilic–hydrophobic characters of these zeolites and ZSM-5 with various Si/Al ratios were evaluated by measurements of immersional heats into water. Adsorption rates and amounts of sodium dodecylsulfate (SDoS) on these zeolites from its aqueous solution were also investigated.

Experimental

Samples used were ZSM-5 zeolites of Mobil Catalysts Corporation of Japan with various Si/Al ratios (Table 1) and Linde SK-40 with a Si/Al ratio of 2.3 (Na-$Y_{4.6}$). The latter was further dealuminated by the procedure similar to that reported by Beyer et al. [13–16]. Original Na-$Y_{4.6}$ was evacuated at 773 K for 2 h, cooled to room temperature in flow of dry nitrogen and then contacted with $SiCl_4$-saturated or -containing nitrogen at the flow rate of 200 cm^3/min. Subsequently, the sample was heated at a rate of 4 K/min to between 623 and 723 K, and was in contact with $SiCl_4$-saturated or -containing nitrogen and kept at the final temperature between 0 to 3 h. The sample was then kept at 623 K for 6 h and cooled down to room temperature in a flow of dry nitrogen. The obtained sample was thoroughly washed in distilled water by means of repeated decantation and Soxhlet extraction.

The Si/Al ratio of the framework structure of samples was determined by the infrared spectra of O–T–O (T: Si or Al) vibration regions according to the empirical equation reported by Sohn et al [17]. The spectrum was taken using a JASCO IR-810 spectrophotometer. The sample was in the form of a wafer prepared from a mixture of the zeolite and KBr (1:100). The wavenumbers were calibrated by use of polystyrene film.

The crystallinities of dealuminated samples were evaluated by measurements of x-ray diffraction patterns, and surface areas and pore structures were investigated by measurements of nitrogen adsorption at 77 K.

Heats of immersion of zeolites into water or *n*-hexane were measured by use of a twin conduction-type calorimeter at 298 K according to a procedure similar to the one reported in [18]. The sample was evacuated at 673 K under 1 mPa for 5 h before the measurement.

The adsorption of SDoS on zeolites from its aqueous solution was measured at 298 K as follows: zeolites (0.05–1.0 g) and 50 ml of SDoS aqueous solution the concentration of which was below 6.94 mmol/l (2000 mg/l) and less than the critical micelle concentration (CMC_{SDoS}: 8.1 mmol/l at 298 K) were put into a 100 ml flask, which was then shaken for 24 h. After the zeolite was separated from the solution was determined by ethyl violet–toluene extraction method. The

Table 1. The composition, Si/Al ratio calculated by IR spectrum or lattice constant, crystallite size and surface area of zeolites prepared

Zeolites	Composition	Si/Al		Crystallite size nm	Surface area m^2/g (dry)
		IR	X-ray		
Na-Y_{64}	$Na_{5.8}Al_{5.8}Si_{186.2}O_{384}$	32			530
Na-Y_{54}	$Na_{6.9}Al_{6.9}Si_{185.1}O_{384}$	27	55	42	490
Na-Y_{47}	$Na_{7.9}Al_{7.9}Si_{184.1}O_{384}$	23			490
Na-Y_{47}	$Na_{7.9}Al_{7.9}Si_{184.1}O_{384}$	23			590
Na-Y_{28}	$Na_{12.9}Al_{12.9}Si_{179.1}O_{384}$	14	15	38	540
Na-Y_{24}	$Na_{14.9}Al_{14.9}Si_{177.1}O_{384}$	12	9.4	32	500
Na-Y_{18}	$Na_{18.9}Al_{18.9}Si_{173.1}O_{384}$	9.1			560
Na-Y_{13}	$Na_{26.0}Al_{26.0}Si_{166.0}O_{384}$	6.4	5.4	48	540
Na-$Y_{4.6}$ (orig.)	$Na_{58.2}Al_{58.2}Si_{133.8}O_{384}$	2.3	3.1	49	720
ZSM-5-1000Na	$Na_{0.14}Al_{0.14}Si_{95.86}O_{192}$*)	670			330
ZSM-5-200Na	$Na_{0.91}Al_{0.91}Si_{95.09}O_{192}$*)	105			280
ZSM-5-70Na	$Na_{2.0}Al_{2.0}Si_{94.0}O_{192}$*)	46.2			350
ZSM-5-50Na	$Na_{3.6}Al_{3.6}Si_{92.4}O_{192}$*)	25.9			320
ZSM-5-25Na	$Na_{6.9}Al_{6.9}Si_{89.1}O_{192}$*)	12.9			260

*)These values were determined by Mobil Catalysts Corp. of Japan

amount of adsorption was determined from the concentration change before and after the adsorption.

Adsorption rates of SDoS on zeolites from its aqueous solution were measured at 298 K. A 100 ml flask containing zeolites (0.03 g – 1.0 g) and 50 ml of 100 mg/l SDoS solution was shaken. 0.1 ml of the solution was collected at a proper interval and the SDoS concentration was determined by a procedure similar to that mentioned above.

Results and discussion

Table 1 shows the composition, Si/Al ratio, crystallite size and surface area of zeolites. The composition was calculated from the Si/Al ratio determined by IR spectrum under the assumption that the zeolitic stoichiometry was kept after the $SiCl_4$ treatment. The highest Si/Al ratio was about 10 times the one of the original Na-$Y_{4.6}$.

It was confirmed by the measurement of x-ray diffraction that the crystallinity of these siliceous zeolites retained after the treatment. However, a slight decrease of the intensity of diffraction peaks was observed due to a partial destruction of the regular crystal structure. The crystallite sizes of these zeolites were determined from the line broadening of (533), (642), and (555) peaks and the average ones are shown in the table and were found to decrease by the treatment. The lattice constant also decreased by the treatment because of smaller ionic diameter of Si^{4+} compared to that of Al^{3+}. The Si/Al ratio was alternatively determined from the value of the lattice constant using the relation reported elsewhere [17] and shown in the table. The ratios agree rather well with those determined by IR except Na-Y_{54}.

The particle size measured by SEM observation was about 1 μm and was unchanged by the treatment.

The shape of N_2 adsorption isotherms on modified Na-Y at 77 K was similar to that of the original Na-$Y_{4.6}$, which indicates that the micropore structure retained without any formation of secondary pore after the modification. However surface areas decreased after the modification, presumably because of a partial destruction of the zeolite structure, which is consistent with the result of x-ray diffraction analysis.

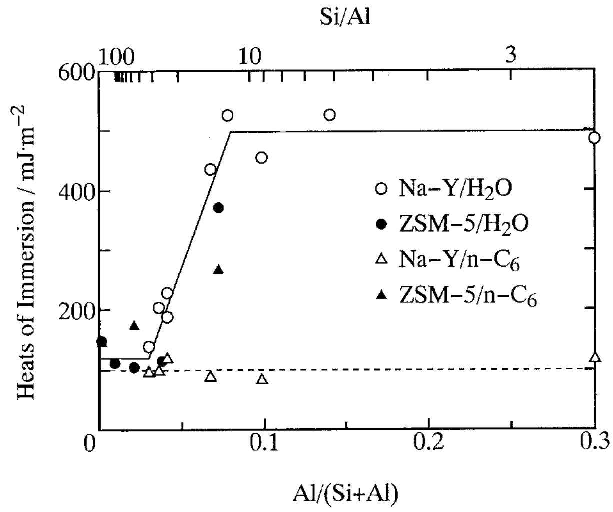

Fig. 1. Heats of immersion of faujasites and ZSM-5 into water or *n*-hexane at 298 K

Heats of immersion of ZSM-5 and Na-Y into water or *n*-hexane at 298 K are shown in Fig. 1. The heats of immersion of zeolites into water have three stages in their variation depending on the Al/(Si + Al) ratio. In the region where the ratio is higher than 0.08, heats of immersion of Na-Y series into water were constant in the value of about 500 mJ/m^2. Heats of immersion of hydrophilic metallic oxides are generally between 150 and 500 mJ/m^2 and those of hydrophobic solid carbons are between 70 and 100 mJ/m^2 [18, 19, 20]. The high value in this stage should be due to the adsorption by specific interaction of polar water molecules on cations on zeolite pore surface. Since the pore volume is limited, the number of water molecules which can interact specifically with cations is limited and vice versa. This may be the reason why the heat value was constant irrespective of the ratio in this stage. The value of 0.08 in the Al/(Si + Al) ratio corresponds to 16 cations per unit cell or 2 cations per large cavity. In the region of the ratio between 0.03 and 0.08, heats of immersion of both Na-Y and ZSM-5 series into water decreased linearly with the ratio. This suggests that the hydrophilicity of zeolites is dependent on the amount of Na^+ or framework anions and is decreased by dealumination-Si insertion process in faujasites. The heats of immersion of ZSM-5 zeolites lie on the same relation, which is indicative that the hydrophilicity is determined

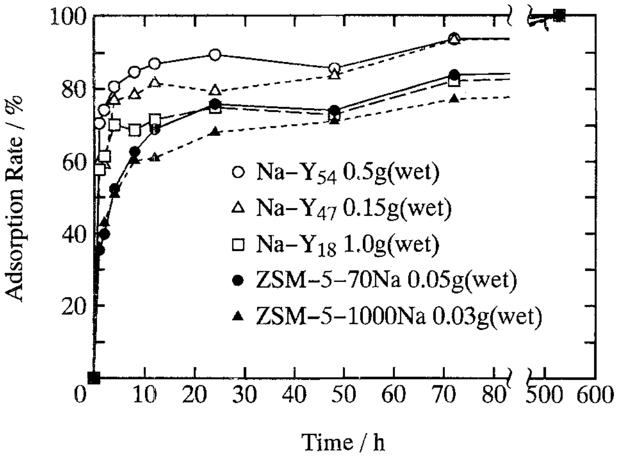

Fig. 2. The rate of SDoS adsorption at 298 K

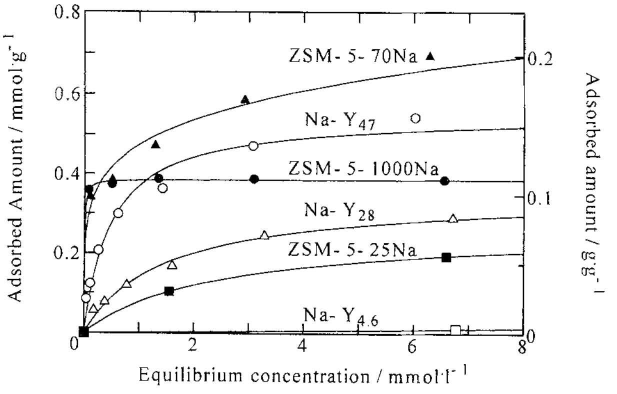

Fig. 3. Adsorption isotherms of SDoS on various zeolites at 298 K

exclusively by the Al/(Si + Al) ratio and not by the zeolite structure. From the increment in heats of immersion in this region, the hydration energy of Na^+ in micropores was calculated to be about 340 kJ/mol, which is lower than the hydration energy of Na^+ in bulk water (400 kJ/mol). This may be due to steric limitation in faujasite micropores. From these results, in case of faujasite zeolites the number of Na^+ ions must be lower than 16 or the Si/Al ratio must be above 10 so as to be hydrophobic.

Below 0.03 in the ratio, the heats of immersion of ZSM-5 series into water were constant and about 120 mJ/m^2. The low value reflects that the immersion proceeds via weak physical interaction between water molecules and almost siliceous zeolite surface.

Heats of immersion of Na-Y series into *n*-hexane were constant and about 100 mJ/m^2 in all range of Al/(Si + Al), suggesting that the interaction between *n*-hexane molecule and zeolite surface is only dispersive. Increased heats of immersion into *n*-hexane in case of ZSM-5 with lower Si/Al ratio may be ascribed to the synergetic effect of the overlapping of adsorption potential of ZSM-5 with smaller pore diameter and increased electrostatic field on the surface.

Results on adsorption rates of SDoS are shown in Fig. 2, the ordinate of which represents a fractional adsorption amount with regard to the saturated one at each interval. The adsorption on all samples was observed to be relatively slow, which can be explained by several facts, i.e., that zeolites have micropores of molecular dimension, molecular size of SDoS is relatively large for the micropore, and the water molecule existing in the micropore inhibits SDoS diffusion in the micropore. Adsorption ratios of SDoS on Na-Y_{54} and Na-Y_{47} which are highly hydrophobic reach habout 95% after 72 h of contact, while those on Na-Y_{18}, which is less hydrophobic, and ZSM-5 reach only about 80% after 72 h. In the initial stage, the adsorption rates of ZSM-5 are low compared with those of hydrophobic Na-Y zeolites, this being due to a smaller pore size and zigzag channel structure of ZSM-5. In the case of Na-Y, the adsorption rates of highly hydrophobic Na-Y_{47} and Na-Y_{54} are higher than that of less hydrophobic Na-Y_{18}. In the latter case, a competitive adsorption between SDoS and water molecules must occur. In cases of highly hydrophobic zeolites such as ZSM-5-70 Na or ZSM-5-1000 Na, the rate is instead affected by the number of cations, suggesting that ion-dipole interaction is also involved in the adsorption process. The order of the rate is similar to that of adsorbed SDoS amount which will be discussed below.

The adsorption rate did not fit the kinetics of Langmuir-type equation, which suggests that SDoS adsorption was governed by pore diffusion. Both adsorption diffusion of SDoS molecules from its aqueous solution into zeolite micropores and desorption diffusion of water molecules from zeolite micropores to outside may be rate-determining steps.

Adsorption isotherms of SDoS on various zeolites at 298 K are shown in Fig. 3. Surfactants concentration is in general below the CMC in actual water pollution and it was reported that the adsorption process changed with the formation of the micelle [21, 22]. Therefore, the isotherms were measured only below the CMC in this study. The adsorption amount attains more than 0.5 mmol/g (about 15 wt % of the zeolite) in case of hydrophobic zeolites, which indicates that the adsorption occurs in micropores of zeolites. Adsorption isotherms on zeolites are of Langmuir type, which is frequently observed in typical zeolite adsorptions, i.e., pore filling adsorption. Zeolite micropores may be filled by either SDoS or water molecules depending on their hydrophobicity. No adsorption occurred on the original Na-$Y_{4.6}$, while the modified Na-Y could adsorb as the Si/Al ratio increased. In Na-$Y_{4.6}$, SDoS adsorption must be inhibited by the presence of water since Na-$Y_{4.6}$ is highly hydrophilic, which is evidenced by its heats of immersion into water. Such a competitive adsorption has often been reported between hydrophilic and hydrophobic adsorbates. Adsorption of phenol on surface-oxygenated carbon black from its aqueous solution was hindered by water molecules, which selectively adsorbed on surface oxygen compounds [23].

The Langmuir constants *a* and *b* of zeolite is shown in Table 2. The Langmuir constant *a* reflects the adsorption interaction and *b* is the saturated adsorbed amount. The constant *a* increases with an increase in the hydrophobicity of zeolites and extremely high value was observed in ZSM-5-1000Na, which corresponds to the initial adsorption isotherm shown in Fig. 3.

The adsorbed amount on Na-Y_{47} was less than that on ZSM-5-1000 Na at low concentration region, but exceeded at higher concentration. However, the adsorbed amount on Na-Y_{28} was smaller than that on ZSM-5-1000 Na at all cocentration regions. From these results, the hydrophobicity of zeolites is more dominant than the type of pore structure in SDoS adsorption from aqueous phase.

Table 2. Langmuir constants of SDoS adsorption on hydrophobic zeolites from its aqueous solution

	a	*b*/mmol · g^{-1}
ZSM-5-1000Na	149	0.386
ZSM-5-70Na	6.49	0.726
ZSM-5-25Na	0.407	0.265
Na-Y_{47}	2.03	0.551
Na-Y_{28}	0.669	0.350
Na-$Y_{4.6}$	–	≈ 0.011

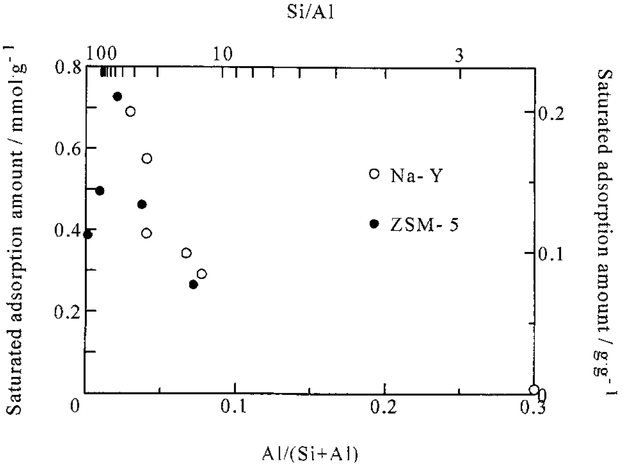

Fig. 4. The relation between Al/(Si + Al) ratio and saturated adsorption amount of SDoS

The relation between saturated adsorbed amounts of SDoS on zeolites (*b*) calculated from the slope of Langmuir plot and the framework Al sites ratio of T-site (T: Si or Al) is shown in Fig. 4. In case of ZSM-5, the adsorption capacity was in the order; 25 Na ≅ 1000 Na < 50 Na ≅ 200 Na < 70 Na. The value of hydrophile–lipophile-balance, HLB_{Davies}, of SDoS is 40 [24], which is fairly high, suggesting that SDoS is of considerably hydrophilic character. Therefore, not only the hydrophobic group of SDoS but also the hydrophilic one should interact with active sites formed by cations and framework negative sites on zeolite surface. The former interaction is by dispersion force and the latter by dipole-electrostatic field one. Then SDoS adsorption on zeolites should depend on the hydrophile-hydrophobe balance of zeolite surfaces. Einick et al. measured adsorptions of ethanol on NaZSM-5 with various Si/Al ratios from its aqueous solution and reported that adsorbed amount became maximum on the zeolite with Si/Al ratio of about 85 [25]. A detailed comparison with the results of immersional heats into water shown in Fig. 1 indicates that the hydrophobic character of zeolites is a prerequisite in order to adsorb SDoS from aqueous solution. However, in case of ZSM-5, it is clear that SDoS adsorption depends on the hydrophile–hydrophobe balance of zeolites. The degree of the

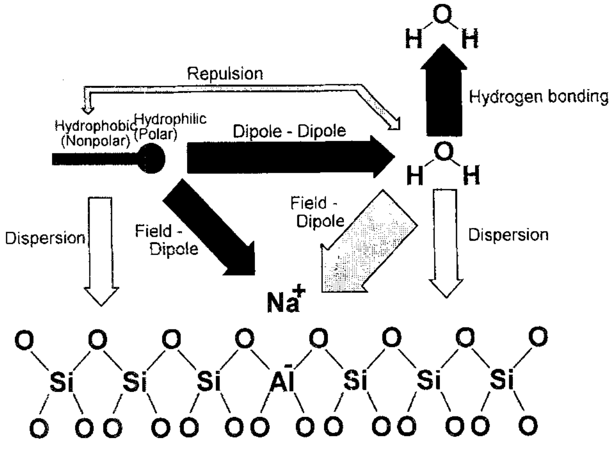

Fig. 5. The scheme of interactions of ternary system; zeolite surface–SDoS–water

increase in adsorbed amount with the Si/Al ratio of Na-Y was observed to be higher than that of ZSM-5. This may be explained by the fact that the pore structure of Na-Y is more advantageous for SDoS adsorption from a viewpoint of its pore size as well as pore volume.

In ternary adsorption system such as an adsorption from an adsorbate solution on a solid, the adsorption force should be affected by many types of interactions: adsorbent-adsorbate, adsorbent-solvent, adsorbate-solvent, adsorbate-adsorbate, and solvent-solvent. In surface active agents, the interaction with adsorbates must be dominated by hydrophobic as well as hydrophilic group. A scheme of the interaction of the ternary system, zeolite surface-SDoS-water, is shown in Fig. 5. In the case of hydrophilic zeolites such as Na-$Y_{4.6}$, the dipole-electrostatic field interaction between water molecule and polar active sites on the zeolite surface is dominant, which is supported by the result of high immersional heats of such zeolites into water. This interaction force decreases with a decrease in the number of cations or anion sites on zeolite framework. In the case of hydrophobic zeolites, the adsorption of SDoS occurs via the dispersive interaction of its hydrophobic group with the zeolite surface and should be facilitated by repulsive interaction of the group with water molecule which is known as "Hydrophobic effect". In water molecules, since their hydrogen bond is stronger than the dispersion force between water and hydrophobic zeolite surface, the adsorption of water on hydrophobic zeolite surface is disadvantageous. High adsorption capacity of SDoS on hydrophobic zeolite must result from these interactions. Hydrophilic group of SDoS interacts with water or polar active site of zeolites by polar interactions. The presence of a maximum in the saturated amount of SDoS adsorption against Al contents may be due to the synergetic effect of these interactions.

In conclusion, the adsorption ability of SDoS from its aqueous solution developed by the modification with $SiCl_4$ of Na-$Y_{4.6}$. The Si/Al ratio of zeolites should be at least 10 for the adsorption. The adsorption amount depended on the hydrophile–hydrophobe balance of zeolites.

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