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Adsorption characteristics of chloroform on modified zeolites from gaseous phase as well as its aqueous solution

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Abstract: Adsorption characteristics of chloroform from its aqueous solution on Na-Y and Li-Na-Y modified by $SiCl_4$ were measured and compared with those on Na-ZSM-5 and Na-Mordenite.

No adsorption occurred on Na-Y with high hydrophilicity, while the siliceous faujasites became capable of adsorption and its amount increased with increase in the Si/Al ratio. Adsorption isotherms are of Langmuir type, suggesting that adsorption proceeds by pore filling. The adsorption amounts expressed in volume on Na-Y with high hydrophobicity corresponded to their pore volumes.

Adsorption characteristics of chloroform from gaseous phase on Na-Y with different Si/Al ratio were also measured. The adsorption capability decreased with increasing Si/Al ratio.

Immersional heats of zeolites into water or chloroform were measured in order to evaluate the surface affinity to both solvents. Immersional heats into water were almost constant (about 500 $mJ \cdot m^{-2}$) for zeolites with their Si/Al ratio below 10. The heats decreased with an increase in the Si/Al ratio above 10, then became almost constant (about 120 $mJ \cdot m^{-2}$) over 30 in their ratio. Heats of immersion of Na-Y series into chloroform were almost constant irrespective of their Si/Al ratio, but decreased slightly when the ratio exceeded 20.

Adsorption characteristics of chloroform could be well related to immersional heats into both solvents.

Key words: Zeolite – modification – chloroform – adsorption

Introduction

Since carcinogenic trihalomethane (THM) was detected in tap water in the USA in 1974, a number of counterplans have been laid down [1–3]. An adsorption removal is one of the methods and hydrophobic active carbon is being used.

An objective of this study is to develop novel adsorbents based on zeolites in order to remove THM from its aqueous solution. The advantage of the use of zeolites is that organics adsorbed in zeolites can be removed by calcination in O_2 flow at high temperature. Typical zeolites such as A- or faujasite-type contain a large number of Al atoms in their framework and are highly hydrophilic [4]. Such hydrophilic characteristics result in adsorption selectivity for polar molecules such as H_2O. Therefore, although zeolites are capable to adsorb a great amount of organics, their adsorbability is easily prevented in the presence of water. In order to overcome such a disadvantage, zeolites must be hydrophobic without any loss of adsorption capacity. The procedure is to remove Al atoms which are responsible for the formation of electrostatic field and for hydrophilic characteristics.

From view points of catalytic applications, several dealumination methods have been carried out in order to obtain chemically and thermally stable zeolites such as hydrothermal [5–7], acidic [8–11], EDTA [12–14], $(NH_4)_2SiF_6$ [15–17] and $SiCl_4$ [18–20] treatments. In particular, $SiCl_4$

treatment has been known to be advantageous from viewpoints of the substitution of Al atoms for Si atoms, high degree of the substitution and low destruction of zeolite framework during the treatment.

In this study, tetrachlorosilane($SiCl_4$)-treated faujasites will be used for the adsorption of chloroform from its aqueous solution. The channel structure of faujasites is three-dimensional and its entrance is large enough for the adsorption of most organic molecules. The surface properties of treated zeolites will be evaluated from pore structure and calorimetric analysis, and related to adsorption behavior. Mordenites and ZSM-5 zeolites are also investigated and compared.

Experimental

Na-faujasite (Na-$Y_{5.5}$: $Na_2O \cdot Al_2O_3 \cdot (SiO_2)_{5.5} \cdot nH_2O$) (Tosoh Corporation), Na-Mordenite (M-10: $Na_2O \cdot Al_2O_3 \cdot (SiO_2)_{9.8} \cdot nH_2O$, –15: $Na_2O \cdot Al_2O_3 \cdot (SiO_2)_{15} \cdot nH_2O$, –20: $Na_2O \cdot Al_2O_3 \cdot (SiO_2)_{20} \cdot nH_2O$) (Tosoh Corporation), and Na-ZSM-5 (ZSM-5-25Na: $Na_2O \cdot Al_2O_3 \cdot (SiO_2)_{25.8} \cdot nH_2O$, –70Na: $Na_2O \cdot Al_2O_3 \cdot (SiO_2)_{92} \cdot nH_2O$, –1000Na: $Na_2O \cdot Al_2O_3 \cdot (SiO_2)_{1340} \cdot nH_2O$) (Mobil Catalysts Corporation of Japan) were used. A so-called SAIZ Na-Y (Si/Al = 5.9 and 7.9) was also used, which was obtained by acidic dealumination of Na-Y with sulfuric acid in the presence of silicilic acid and subsequent Na-exchange [21, 22]. The crystallinity was found to be retained and Si insertion was observed to occur during this treatment.

Li-Na-Y (Li ion exchanged Na cation type Y zeolite) was prepared as follows: 50 g of Na-$Y_{5.5}$ was repeatedly treated in 1 l of $LiNO_3$ aqueous solution of 0.35, 0.80 and 1.02 mM at 353 K for each 24 h. After Li-ion exchange, the sample was decanted and filtered, then dried at 383 K.

Na-$Y_{5.5}$, Li-Na-$Y_{5.5}$ and SAIZ Na–Y were further modified by the dealumination-silicon exchange reaction by the procedure similar to that reported by Beyer et al. [18–20].

About 5 g of zeolites was dehydrated *in vacuo* at 673 K for 12 h and contacted with $SiCl_4$-saturated or contained nitrogen at a flow rate of 200 ml/min at between 623 and 793 K. The sample was then kept at 623 K for 24 h in flow of dry nitrogen and cooled down to room temperature. The obtained sample was thoroughly washed in distilled water by means of repeated decantation and Soxhlet extraction for a week.

The Si/Al ratio of the framework structure of samples was mainly determined by the infrared spectra of O–T–O vibration range according to the empirical equation reported by Sohn et al. [23]. 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 taken using a Philips PW1729 x-ray generator.

Surface areas and pore structures were investigated by measurements of nitrogen adsorption at 77 K on samples evacuated at 673 K for 5 h.

The adsorption of chloroform from gaseous phase was measured by gravimetric method at 303 K on samples evacuated at 673 K for 5 h.

The adsorption of chloroform from its aqueous solution was measured at 298 K as follows: 0.1 g of zeolites and 50 ml of the aqueous solution, the concentration of which was between 1.77 mmol/l and 56.5 mmol/l, were put into a 75 ml brown vial flask, which was then shaken for 24 h in thermostated chamber at 298 K. The zeolite was separated from the solution by a centrifuge (3000 rpm, for 5 min) and the concentration of the supernatant solution was determined by gas chromatograph with FID detector. The gas chromatogram was taken using a Shimazu GC-7AG with a glass column 3 m × 2.6 mm i.d. packed with 20% squalane chtromosorb WAW of 80/100 mesh. The amount of adsorption was determined from the concentration change before and after the adsorption.

Heats of immersion of zeolites into chloroform were measured at 298 K by use of a conduction-type calorimeter according to the procedure similar to the one reported elsewhere [24]. The sample was evacuated at 673 K under 1 mPa for 5 h before the measurement.

Results and discussion

Table 1 shows preparation conditions and chemical compositions of dealuminated faujasites.

Table 1. Preparation condition, Si/Al ratio, Al/(Si+Al) ratio, lattice constant a_0 and water adsorption amount of faujasite samples used.

Sample	Temp/K		Si/Al	Al/(Si+Al)	a_0
	initial	final			nm
Na-Y$_{5.5}$	–	–	2.7	0.25	2.463
Na-Y$_{12}$ (SAIZ-5.9)	–	–	5.9	0.15	2.447
Na-Y$_{16}$ (SAIZ-7.9)	–	–	7.9	0.12	–
Na-Y$_{42}$*^{2}	523	623	21	0.047	2.429
Na-Y$_{78}$*^{1}	513	773	39	0.025	2.427
Na-Y$_{104}$*^{1}	513	773	52	0.019	2.427
Na-Y$_{130}$*^{1}	523	733	65	0.015	2.427
Na-Y$_{224}$*^{4}	523	783	112	0.0088	2.424
Na-Y$_{344}$*^{5}	523	793	172	0.0058	2.427
ZSM-5-25Na	–	–	12.9	0.072	–
ZSM-5-70Na	–	–	46.2	0.021	–
ZSM-5-1000Na	–	–	670	0.0015	–
M-10	–	–	4.90	0.17	–
M-20	–	–	10.0	0.091	–

Starting materials of dealumination samples were as follows:
*1: Na-Y$_{5.5}$
*2: Na-Y$_{12}$ (SAIZ-5.9)
*3: Na-Y$_{16}$ (SAIZ-7.9)
*4: Li-Na-Y$_{12}$ (SAIZ-5.9)
*5: Li-Na-Y$_{16}$ (SAIZ-7.9)

The lattice constants a_0 were determined as an average of (511), (440) and (642) peaks of x-ray diffraction patterns. These peaks shifted to higher angle and the lattice constants decreased with dealumination because of smaller ionic diameter of Si^{4+} compared to Al^{3+}. These results support that the Al atoms in zeolite framework were substituted for Si atoms by $SiCl_4$ treatment [25]. The diffraction profile intensities of some modified zeolites decreased, which indicate that partial destruction occurred in their structure.

Several methods to determine Al contents of zeolites have been reported; chemical analysis, ^{29}Si-MAS-NMR, IR spectroscopy, x-ray diffraction and so on. In this study, Si/Al ratios of modified Na-Y were determined by means of IR spectroscopy and x-ray diffraction, and compared. The bands attributed to lattice vibrations of zeolite framework are observed in the range of 300–1300 cm^{-1}, some of which prove to shift with Al content in the zeolite framework [26]. A comparison plot of Al/(Si+Al) of samples determined by both methods is shown in Fig. 1. They almost agree, but the Al/(Si+Al) determined by x-ray diffraction is smaller than that by IR spectroscopy. The Al(Si+Al) of Na-Y$_{5.5}$ determined by chemical method is 0.26, which is in agreement with the result by IR spectroscopy. In this work, the Al/(Si+Al) or Si/Al ratio determined by IR spectroscopy will be used. The subscript number

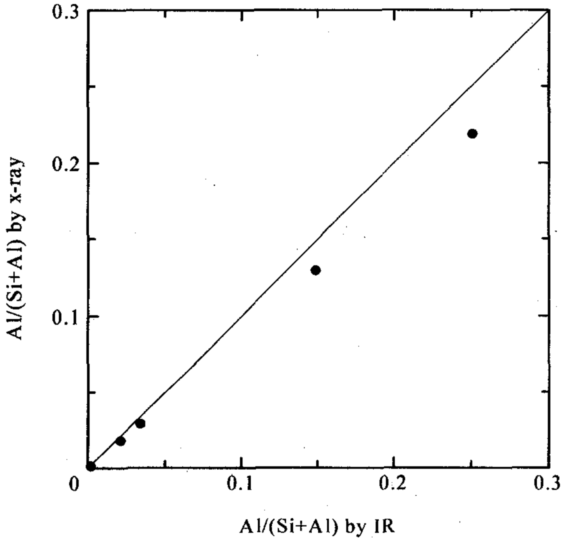

Fig. 1. A comparison plot of the Al(Si+Al) of faujasites determined by IR and x-ray

of the sample name represents twice the Si/Al ratio.

When Na-$Y_{5.5}$ was used as the starting material of $SiCl_4$ treatment, the upper limit of Si/Al ratio of treated Na-Y which had relatively high crystallinity was, at most, about 20. This limit might be explained by the deposition of nonvolatile $Na(AlCl_4)$ complex into the zeolite pores [19].

Since $Li(AlCl_4)$ complex vaporizes more easily than $Na(AlCl_4)$, the dealuminated Li-Na-Y can be expected to have higher Si/Al ratio without crystallinity loss [20]. In fact, when Li-Na-Y was used as the parent material of the treatment, dealuminated Li-Na-Y with Si/Al ratio of about 50 could be obtained. However, the low exchange level of Li^+ due to its high hydration energy [27–29] prevents more efficient dealumination.

The highest level of Al removal could be obtained from SAIZ samples and attained about 98% of Al atoms contained in conventional Na-$Y_{5.5}$. In particular, when Li-exchanged SAIZ was used as the starting material, the obtained sample had Si/Al ratio as high as 170. This can be ascribed to the synergetic effect of high stability of SAIZ and Li exchange.

Saturated amount of water adsorption, which was determined by standing dehydrated samples in water vapor in the vicinity of saturation, became lower as the dealumination proceeded, indicating that Na-Y changed in their surface characteristic from hydrophilic to hydrophobic by $SiCl_4$ treatment.

N_2 adsorption isotherms on some Na-Y at 77 K are shown in Fig. 2. The isotherms of modified zeolites are similar in their shape to that of the parent Na-$Y_{5.5}$, which suggests that the essential pore structure was retained after $SiCl_4$ treatment. The isotherms are of Type I according to BDDT classification, indicating that the adsorption proceeds by pore filling.

The surface areas calculated by use of BET equation and pore volumes determined by adsorbed amount of N_2 at $P/P_0 = 0.99$ are shown in Table 2. In certain modified zeolites they were found to be rather lower than those of the parent Na-$Y_{5.5}$. This may be due to the partial destruction of the zeolite framework by dealumination as mentioned above and/or to the blocking of zeolite pores by Al species existed in extra-framework [19, 30].

Adsorption isotherms of chloroform from gaseous phase on several zeolites are shown in Fig. 3. These isotherms are of typical Langmuir type and

Table 2. Pore volume and BET surface area of faujasites used

Sample	Al/(Si+Al)	Pore volume $ml \cdot g^{-1}$	BET surface area $m^2 \cdot g^{-1}$
Na-$Y_{5.5}$	0.25	0.47	720
Na-Y_{12}	0.15	0.33	620
Na-Y_{42}	0.047	0.43	710
Na-Y_{78}	0.025	0.38	620
Na-Y_{104}	0.019	0.32	540
Na-Y_{130}	0.015	0.29	460
Na-Y_{224}	0.0088	0.37	580
Na-Y_{344}	0.0058	0.31	430

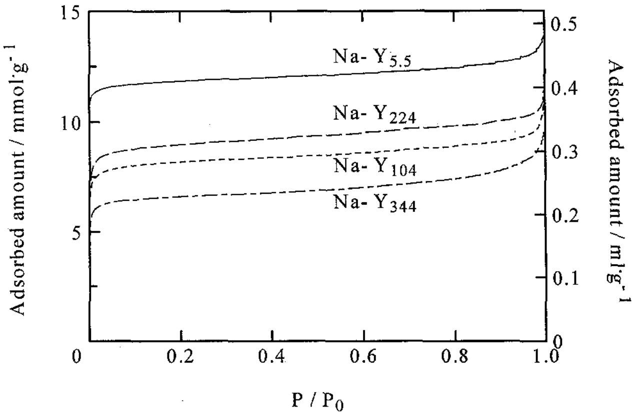

Fig. 2. Adsorption isotherms of N_2 on faujasites at 77 K

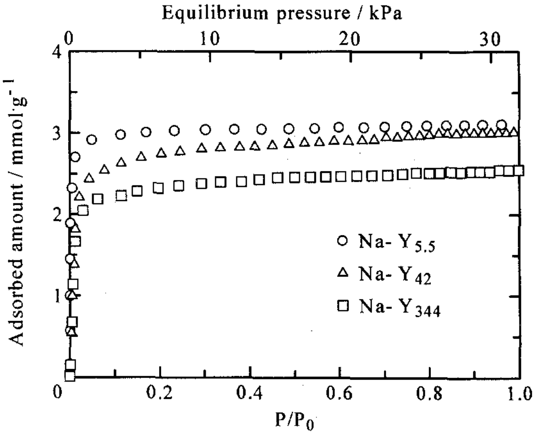

Fig. 3. Adsorption isotherms of chloroform from gaseous phase on faujasites at 303 K

Table 3. Langmuir constants *a* and *b* of chloroform adsorption from gaseous phase on the parent and dealuminated faujasites.

Sample	Al/(Si+Al)	*a*	*b* $\text{mmol}\cdot\text{g}^{-1}$
Na-$Y_{5.5}$	0.25	0.80	3.12
Na-Y_{42}	0.047	0.22	3.04
Na-Y_{344}	0.0058	0.20	2.59

the adsorption amount decreased slightly with a decrease in the Al(Si+Al) ratio. The Langmuir constants *a* and *b* were listed in Table 3. The constant *a*, which reflects adsorption affinity, also decreased with a decrease in the Al/(Si+Al). Since chloroform molecule can interact by its dipole with zeolite surface field, a decrease in Al atoms, which are the origin of the electrostatic field, should affect the adsorption behavior. Only a slight decrease in the adsorption amount indicates that the adsorption proceeds mainly by dispersive interaction.

Adsorption isotherms of chloroform on the parent and modified Na-Y from its aqueous solution at 298 K are shown in Fig. 4. Since it was verified that adsorption completed within 24 h, the adsorption amount was measured after this interval. No adsorption occurred on the original Na-$Y_{5.5}$, while the siliceous faujasites became capable for the adsorption and its amount increases with a decrease in the Al/(Si+Al) ratio or with an increase in the Si/Al ratio. The original Na-$Y_{5.5}$ contains a great number of Na cations as well as framework anion sites, which induces strong adsorption affinity for polar molecules such as water by dipole-electrostatic field interaction. The high hydrophilicity of Na-$Y_{5.5}$ is evidenced by its heats of immersion into water [4]. On hydrophilic zeolites, the chloroform adsorption should be inhibited from its aqueous solution. Adsorption isotherms of chloroform can be classified to type I, which indicates that the adsorption occurred typically into zeolite pores and the adsorbate – adsorbent interaction is rather strong. Saturated amounts of chloroform on zeolites calculated from the slope of Langmuir plot of the isotherms depend significantly on Al/(Si+Al) or Si/Al ratio as shown in Fig. 5. The saturated amount on the parent Na-$Y_{5.5}$ was only about 2% of its pore volume on which water should be selectively adsorbed. The amount increased with a decrease in the Al content in the region between 0.05 and 0.03 in Al/(Si+Al) indicating that zeolites become more and more hydrophobic. Below 0.03 in Al/(Si+Al), the saturated amount became almost constant and was equal to their pore volume. Zeolites in this region became highly hydrophobic and tended to adsorb selectively chloroform, and water adsorption was almost prevented. In this adsorption system, repulsion force between chloroform and water as well as low affinity of water to hydrophobic zeolite should be the driving force for selective adsorption of chloroform.

Adsorption isotherms of chloroform on ZSM-5 or mordenite from its aqueous solution at 298 K

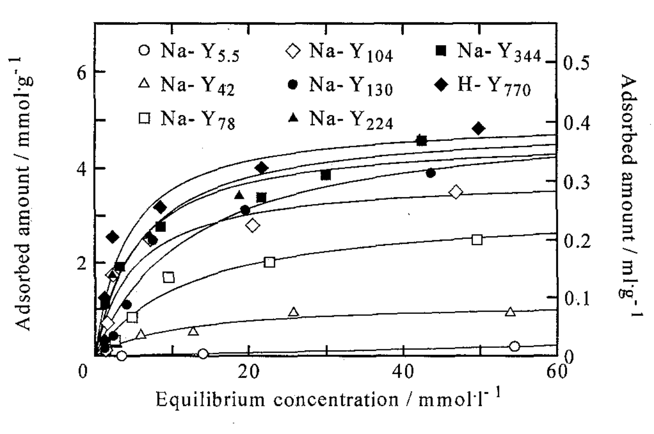

Fig. 4. Adsorption isotherms of chloroform from its aqueous solution on faujasites at 298 K

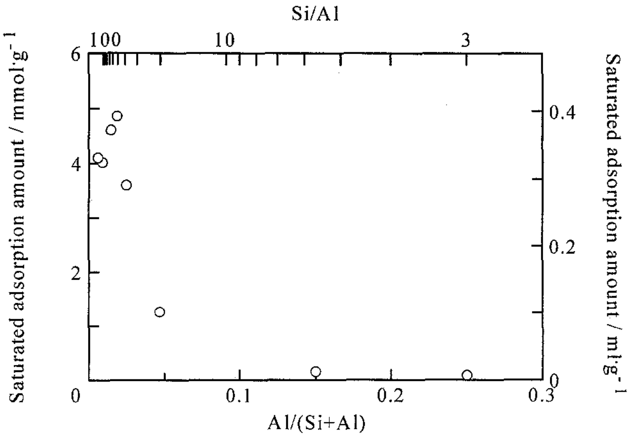

Fig. 5. A relationship between Al/(Si+Al) ratio of faujasites and saturated adsorption amount of chloroform from its aqueous solution

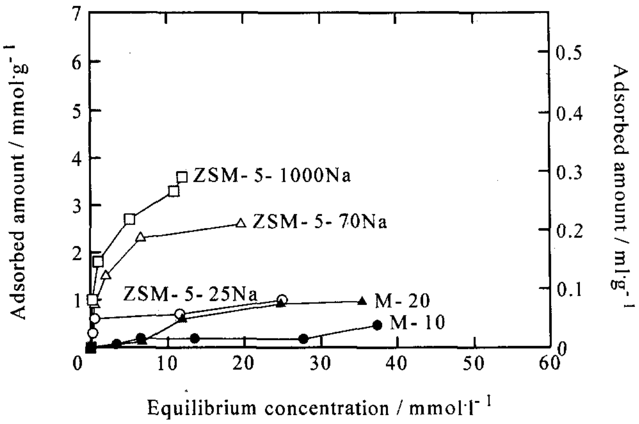

Fig. 6. Adsorption isotherms of chloroform from its aqueous solution on ZSM-5s and mordenites at 298 K

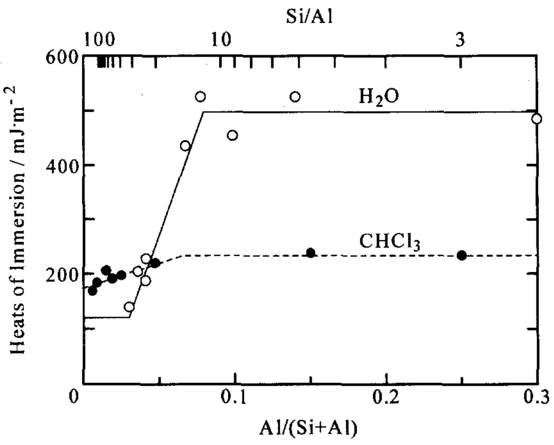

Fig. 7. Heats of immersion of faujasites into water [31] or chloroform at 298 K

are shown in Fig. 6. The adsorption amount increased with an increase in the Si/Al ratio in both zeolites. These results indicate that only the hydrophobicity of zeolite surface affects the chloroform adsorption in the presence of water.

Heats of immersion of Na-Y into water [31] or chloroform at 298 K are shown in Fig. 7. They are expressed per unit surface area determined by N_2 adsorption. The heats of immersion into water varied with Al/(Si+Al) or Si/Al ratio in three ways. In the range where the Al/(Si+Al) ratio is higher than 0.08, heats of immersion were almost constant and about $500 \mathrm{mJ \cdot m^{-2}}$. Heats of immersion of hydrophilic metallic oxides are generally between 150 and 500 $\mathrm{mJ \cdot m^{-2}}$ and those of hydrophobic solid carbons are between 70 and 100 $\mathrm{mJ \cdot m^{-2}}$ [24, 31, 32]. The high value in this stage should be due to the adsorption by specific interaction of polar water molecules on Na cations on zeolite pore surface. Since the pore volume is limited, the number of water molecules which can interact specifically with Na cations is limited. This may be the reason why the heat values were almost constant irrespective of the ratio in this stage. In the region of the ratio between 0.03 and 0.08, the heats of immersion into water decreased linearly with the ratio. This confirms that the hydrophilicity of zeolites is dependent on the Al content in their framework and decreased by dealumination – Si insertion process. Below 0.03 in the ratio, the heats of immersion into water were constant of about 120 $\mathrm{mJ \cdot m^{-2}}$. 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 chloroform did not significantly change in all range of Al/(Si+Al), but the heats decreased slightly below 0.06 in the ratio. This suggests that the interaction between chloroform molecule and zeolite surface is mainly dispersive and the contribution of dipole - field interaction is rather small.

By comparison of these results with those of chloroform adsorption from aqueous solution, several points should be noted. Firstly, distinct chloroform adsorption could be observed only on zeolites with Al/(Si+Al) below 0.08 of which immersional heats of water became lower. Secondly, on zeolites of which immersional heats into water and chloroform were reversed enhanced adsorption of chloroform could be observed. On fully hydrophobic zeolites, their pores were filled only by chloroform even in the presence of water.

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