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Catalysis at the Toluene/Water Interface: Octadecyl Immobilized H-ZSM-5 Catalyst Promoted Hydrolysis of Water-Insoluble Esters

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Octadecyltrichlorosilane-treated H–ZSM-5, abbreviated as H–ZSM-5–C_{18}, resulted in an effective catalyst for the hydrolysis of water-insoluble esters in toluene–water solvent system. These floated at the interface of the two liquids. The H–ZSM-5–C_{18} catalyst showed ca. 60 times the activity of H–ZSM-5 for the hydrolysis of dodecyl acetate. Acid strength of H–ZSM-5 in water ($-5.6 < Ho \leq -3.0$) was maintained even after the treatment with octadecyltrichlorosilane. The treatment renders H–ZSM-5 lipophylicity and provides a quasi-lipid phase on the surface. The shape-selective properties of H–ZSM-5–C_{18} catalyst were observed for the hydrolysis of aliphatic esters with straight chains.

INTRODUCTION

Zeolites draw much attention due to its remarkable shape-selective properties besides acid–base property. Hence, zeolites have been used for organic syntheses (1). Examples are shown in photolysis of alkanophenones (2) and dibenzyl ketone (3), ring-opening reaction of 2,3-epoxy alcohols (4), alkylation of toluene (5), and isomerization of *m*-xylene (6), where the substrate molecules react in the cavity or channel with suppression of translational movement. H–ZSM-5 zeolite is a strong solid acid in aqueous solution (7) and is expected to have a high activity as a catalyst in hydrolysis.

Namba *et al.* have reported the hydrolysis of dilute ethyl acetate in aqueous solution by use of high-silica zeolites as a catalyst (7). The catalyst was effective for water-soluble esters such as ethyl acetate. We have reported briefly that octadecyl-silane-treated H–ZSM-5 catalyst, abbreviated as H–ZSM-5–C_{18}, showed a new type of interface catalysis, where an acceleration of the hydrolysis of the water-insoluble esters was observed (Eq. [1]) (8). This study provides a new method for the utilization of zeolites, and the details of the results are reported in this paper.

$$RCOOR' + H_2O \xrightarrow[\text{Toluene/H}_2\text{O}]{\text{H-ZSM-5-C}_{18}} RCOOH + R'OH \quad [1]$$

EXPERIMENTAL

Materials

ZSM-5s (Mobile Oil Co., distributed as "standard" catalyst samples from the Catalysis Society of Japan), zeolites of Y type (Y-9) and mordenite type (Z-HM) ("standard" catalyst samples of the Catalysis Society of Japan), zeolites of A type (A-4) and faujasite type (F-9) (Wako Chemicals), and SiO_2–Al_2O_3 (a "standard" catalyst sample of the Catalysis Society of Japan (JRC-SAL-2; 13.8% alumina, Na_2O content 0.012 wt%)) were dried at 110°C for a day and stored in a desiccator.

All the zeolites were powder and their chemical properties are listed below.

ZSM-5-25: SiO_2 content 88.37 wt%, Al_2O_3 content 6.1 wt%, Na content 0.03 wt%;

ZSM-5-70: SiO_2 content 92.7 wt%, Al_2O_3 content 1.7 wt%, Na content 0.82 wt%;

ZSM-5-1000: SiO_2 content 97.66 wt%, Al_2O_3 content 0.133 wt%, Na content 0.0305 wt%;

Z-HY4.8: SiO_2 content 75.15 wt%, Al_2O_3 content 24.43 wt%, Na_2O content 0.20 wt%;

Z-HY5.6: SiO_2 content 72.8 wt%, Al_2O_3 content 22.0 wt%, Na_2O content 3.5 wt%;

Z-HM10: SiO_2 content 83.7 wt%, Al_2O_3 content 14.3 wt%, Na_2O content 0.12 wt%;

Z-HM15: SiO_2 content 88.0 wt%, Al_2O_3 content 10.0 wt%, Na_2O content 0.06 wt%;

Z-HM20: SiO_2 content 91.0 wt%, Al_2O_3 content 7.76 wt%, Na_2O content 0.06 wt%;

A-4: Si/Al atomic ratio 1.0, through 200 mesh;

F-9: Si/Al atomic ratio 1.3, through 200 mesh.

All silylating reagents were guaranteed grade, purchased from Tokyo Kasei Kogyo Co., Ltd.

All Hammett indicators, Neutral red (pK_a = +6.8), Methyl red (pK_a = +4.8), *p*-dimethylaminoazobenzene (pK_a = +3.3), benzeneazodiphenylamine (pK_a = +1.5), dicinnamalacetone (pK_a = −3.0), benzalacetophenone

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($pK_a = -5.6$), and anthraquinone ($pK_a = -8.2$), were reagent grade, purchased from Tokyo Kasei Kogyo Co., Ltd.

Esters were all guaranteed grade, purchased from Tokyo Kasei and Wako Chemicals, and used without further purification. Organic solvents were all guaranteed grade. Toluene was dried over calcium hydride, and methanol and ethanol were dried over molecular sieves prior to use for the catalyst preparation. Other materials were commercially available and used as obtained.

Catalyst Preparation

Each H-zeolite was prepared by a conventional cation exchange procedure using 1 mol liter^{-1} NH_4Cl aqueous solution followed by calcination in air at 500°C. Measurements of X-ray diffraction of A-4 and F-9, which have thermal instability of their ammonium forms, suggest that the structures of both have been maintained after the treatment although some decomposition is evident.

An octadecyl immobilized zeolite (abbreviated as H–zeolite–C_{18}) was prepared by treating H-type zeolite with octadecyltrichlorosilane (9). Typically, H–ZSM-5-70 (Si/Al atomic ratio = 39.0)(2.0 g), octadecyltrichlorosilane (0.39 g, 1.0 mmol), and toluene (60 ml) were put in a dry 100-ml flask equipped with a condenser and drying tube. The mixture was refluxed for 12 h, then methanol (6.4 g, 200 mmol) was added and refluxed for additional 3 h. The mixture was then filtered through a membrane filter and the solid was washed with distilled water (100 ml × 4), followed by toluene (100 ml × 4). Further, the solid was washed with toluene by means of a Soxhlet extractor for a day, and then dried overnight at 80°C.

Octadecyl-ethoxysilane reagents were also used for the preparation of the immobilized zeolite (abbreviated as H–zeolite–$C_{18}(E_tO)$) in the same manner described above except that methanol was replaced with ethanol.

IR and TG–DTA Measurements

The spectra of the zeolite treated with octadecyltrichlorosilane were measured on a JASCO FT/IR 7000 infrared spectrometer by the diffuse reflection technique as a powder.

DTA and TG curves of zeolite samples were obtained simultaneously from room temperature to 800°C with a Rigaku–Denki 8076D TG–DTA analyzer. About 30 mg of the samples were packed in a platinum crucible of 5 mm diameter and 5 mm height. Measurements were made in a dynamic atmosphere of air or argon flowing upward around the vertical holder unit at the rate of 100 ml min^{-1}. As a reference material α-Al_2O_3 was used. Temperature and differential temperature were measured by a pair of Pt + Pt-13% Rh thermocouples.

Procedure of Hydrolysis and Analysis

A typical example of the hydrolysis of ester is illustrated. H–ZSM-5-70–C_{18} (40 mg) and octyl acetate (2.5 mmol, 429 mg) were added to a mixture of toluene (5.0 ml) and distilled water (5.0 ml) in a 50-ml flask, and the suspension was refluxed.

Aliquots of the reaction mixture in the toluene layer and water layer were analyzed on a Yanagimoto Model G900 gas chromatograph with PEG 20M packed column, Chromosorb 101 packed column, and/or MS capillary column. All the reaction products were identified as being identical with standards.

Acid Strength

Acid strength of the zeolite catalysts in water was measured in the following manner: 20 mg of the catalyst and 10 ml of distilled water were put into a flask, 2 drops of 2% ethanol solution of Hammett indicator was added to the water, and then the mixture was allowed to stand for 12 h at room temperature with occasional shaking. The acid strength was determined visually from the color change of the indicator adsorbed on the catalyst.

Partition Coefficient

About 30 mg of each ester was added in a water (5.0 ml) and toluene (5.0 ml) mixture and was allowed to stand for 2 h or overnight at 25°C in a shaker. The amount of the ester in each solvent was determined by GLC analysis.

RESULTS AND DISCUSSION

Fixation of Octadecylsilyl Group

H–ZSM-5 was treated with octadecyltrichlorosilane to provide lipophylicity. To confirm the attachment of the octadecylsilyl group on H–ZSM-5-70–C_{18}, the treated sample was analyzed by IR spectroscopy. Changes of the IR absorption spectra by the treatment with octadecyltrichlorosilane are listed in Table 1. The absorptions due to the alkyl group attributable to the octadecylsilyl group appeared and the absorptions at 1000–1100 cm^{-1} due to the stretching vibration of Si–O were increased slightly, whereas the absorptions due to the OH group of the zeolite were decreased. These data qualitatively indicate that the octadecylsilyl group was fixed certainly on the H–ZSM-5-70–C_{18}.

The results for the TG–DTA measurement are listed in Table 2. Marked weight loss from H–ZSM-5-70–C_{18} was observed in the ranges of 72 to 208°C and of 208 to 400°C, while that from H–ZSM-5-70 was primarily in the range 72 to 208°C. DTA analysis indicates that decomposition of the octadecylsilyl group on the zeolite

TABLE 1

Changes of IR Spectra of H–ZSM-5-70 by the Treatment with Octadecyltrichlorosilane

Band (cm^{-1})			
Appearance or increase in intensity		Decrease in intensity	
$\nu(CH_3)$	2960	ν(Si–OH)	3300–3600
$\delta(CH_3)$	1460	δ(Si–OH)	820
$\nu(CH_2)_n$	720		
ν(Si–O)	1000–1110		

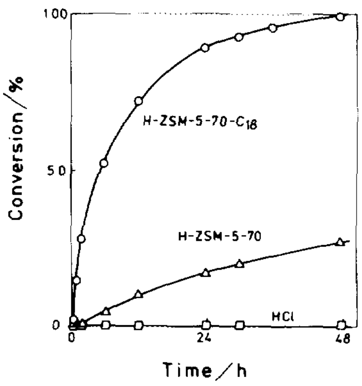

FIG. 1. Reaction profiles for the hydrolysis of octyl acetate. Catalysts (160 mg) and octyl acetate (0.49 mmol, 84 mg) were added to a toluene (20 ml) and water (20 ml) mixture, and the suspension was refluxed. In the case of HCl catalyst, 1 *N* HCl (0.46 g, 0.44 mmol) was added.

started at 208°C, and maximized at 325°C. Numbers of the octadecylsilyl group per unit cell of H–ZSM-5-70–C_{18} ($H_2Al_{2.4}Si_{93.6}O_{192}$; $FW = 5767.46$) can be determined from the decreased weight of TG curves. Taking into account the amount of adsorbed water, about one molecule of the octadecylsilyl group was attached per unit cell of the zeolites prepared by use of both octadecyltrichlorosilane and octadecyltriethoxysilane.

Reaction Profile of the Hydrolysis of Octyl Acetate

Hydrolysis of octyl acetate in the refluxing mixture of toluene–water system was carried out using H–ZSM-5-70–C_{18}. In the system H–ZSM-5-70–C_{18} catalyst floated at the toluene–water interface; in comparison, the nonalkylated H–ZSM-5-70 was suspended in the water. Reaction profiles of the hydrolysis are illustrated in Fig. 1. The H–ZSM-5-70–C_{18} hydrolyzed the octyl acetate to produce octanol in the toluene layer and acetic acid in the water layer quantitatively after 48 h. Only 30% of the octyl acetate was hydrolyzed by H–ZSM-5-70 under the same conditions. When HCl was used as the catalyst, virtually no hydrolysis occurred (0.39% conversion after 48 h). No reaction other than hydrolysis was observed. Octyl acetate is practically insoluble in water (partition coefficient K = ca. 3×10^5, as shown in Table 5). Immobilization of the octadecylsilyl group on solid H–ZSM-5 affected the hydrolysis of water-insoluble octyl acetate to produce octanol in the organic phase and acetic acid in the aqueous phase effectively.

Rate Expression

Kinetic studies were made for the hydrolysis of octyl acetate. Initial rates of the hydrolysis were measured within the range of 5% conversion. The dependence of the initial rate of the reaction on the amounts of the octyl acetate and H–ZSM-5-70–C_{18} is shown in Figs. 2 and 3, respectively. These figures show that the rate was propor-

TABLE 2

Decreased Weight Based on the TG Curves

	72–208°C	208–800°C		
H–ZSM-5-70	Adsorbed water (wt%)	Adsorbed water + C_{18} (wt%)	C_{18} (wt%)[a]	C_{18}/H–ZSM-5
Untreated	4.031	1.262[b]	0	0
H–ZSM-5-70–C_{18}[c]	4.276	6.956	5.694	1.08[d]
H–ZSM-5-70–C_{18}[e]	5.243	7.257	5.995	1.06[f]

[a] Weight percent of octadecylsilyl group calculated by subtracting 1.262 wt% from the weight loss of H–ZSM-5-70–C_{18} at the temperature range 208–800°C.

[b] Due to adsorbed water.

[c] Treated with octadecyltrichlorosilane.

[d] Molar ratio of octadecyldimethoxysiloxy group/H–ZSM-5.

[e] Treated with octadecyltriethoxysilane.

[f] Molar ratio of octadecyldiethoxysiloxy group/H–ZSM-5.

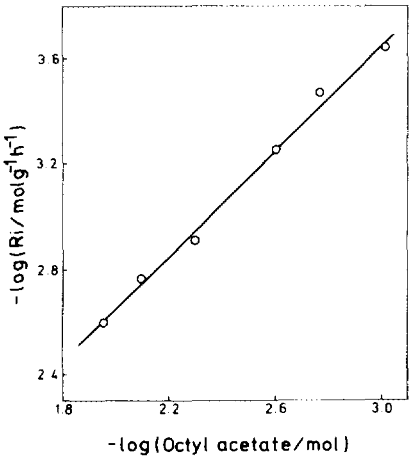

FIG. 2. Dependence of the initial rate R_i of hydrolysis on the amount of octyl acetate.

tional to the amount of the octyl acetate and of the H-ZSM-5-70-C_{18} catalyst. The kinetic order was 1.0 with respect to each of the variables. Then the rate expression

$$Ri = k\,[\text{ester}][\text{H-ZSM-5-70-C}_{18}] \qquad [2]$$

was obtained, where k, [ester], and [H-ZSM-5-70-C_{18}] are the rate constant, the concentration of octyl acetate in toluene, and the amount of H-ZSM-5-70-C_{18}, respectively.

Effective Zeolite

Various types of zeolites were used for the hydrolysis of water-soluble methyl acetate, and the results are summarized in Table 3. The H-ZSM-5-C_{18} series exhibited higher activity, especially H-ZSM-5-70-C_{18}, which had the highest activity. In the case of the same type of zeolites, the higher Si/Al ratio of zeolite exhibits higher activity; however, the maximum activity was present at Si/Al = 7.5 with H-Z-HM type of zeolite and at Si/Al = 39 with H-ZSM-5, respectively. These findings were quite similar to those of the hydrolysis of ethyl acetate over other dealuminated zeolite catalysts (7).

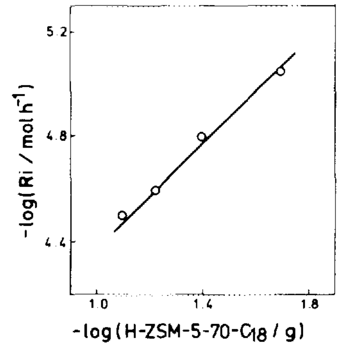

FIG. 3. Dependence of the initial rate R_i of hydrolysis on the amount of H-ZSM-5-70-C_{18}.

TABLE 3

Hydrolysis of Methyl Acetate over Various Zeolites[a]

Zeolite[b] (type)	Si/Al[c]	R_i[d] (10^{-4} mol g^{-1} h^{-1})
None	—	0.05[e]
H-A-4-C_{18} (4A type)	1.0	0.04
H-F-9-C_{18} (Faujasite type)	1.3	0.14
H-Z-HY4.8-C_{18} (Y type)	2.6	0.53
H-Z-HY5.6-C_{18} (Y type)	2.8	0.49
H-Z-HM10-C_{18} (Mordenite type)	4.9	0.81
H-Z-HM15-C_{18} (Mordenite type)	7.5	15.52
H-Z-HM20-C_{18} (Mordenite type)	10.1	15.14
H-ZSM-5-25-C_{18}	12.3	12.35
H-ZSM-5-70-C_{18}	39.0	21.26
H-ZSM-5-1000-C_{18}	543.3	6.29

[a] Methyl acetate (6.2 mmol: 483 mg) and zeolite (40 mg) were used. Other conditions are as in the main text.

[b] Zeolite-C_{18} represents the zeolite treated with octadecyltrichlorosilane.

[c] The Si/Al atomic ratios of zeolites were calculated on the basis of the SiO_2 and Al_2O_3 contents.

[d] Initial rate of hydrolysis.

[e] The assumption that 40 mg of the zeolite would be used.

Octyl acetate was chosen as a representative of water-insoluble esters and was subjected to hydrolysis over various types of zeolites, and the results are summarized in Table 4. H-ZSM-5-70-C_{18} exhibited much higher activity than the other types of zeolites.

Hydrolysis of Various Esters

H-ZSM-5-70-C_{18} was an effective catalyst for the hydrolysis of both water-soluble and -insoluble esters. The

TABLE 4

Hydrolysis of Octyl Acetate over Various Zeolites[a]

Zeolite[b] (type)	R_i[c] (10^{-4} mol g^{-1} h^{-1})
None	0.00[d]
H-F-9-C_{18} (Faujasite type)	0.04
H-Z-HY4.8-C_{18} (Y type)	0.24
H-Z-HM15-C_{18} (Mordenite type)	0.59
H-Z-HM20-C_{18} (Mordenite type)	0.33
H-ZSM-5-70	0.36
H-ZSM-5-70-C_{18}	5.62
H-ZSM-5-1000-C_{18}	0.36

[a] Octyl acetate (2.5 mmol; 429 mg) and zeolite (40 mg) were used. Other conditions are as in the text.

[b] Zeolite-C_{18} represents the zeolite treated with octadecyltrichlorosilane.

[c] Initial rate of hydrolysis.

[d] The assumption that 40 mg of the zeolite would be used.

TABLE 5

Hydrolysis of Various Esters[a]

RC(=O)OR′		Amount of ester (mmol)	R_i^b (10^{-4} mol g^{-1} h^{-1})		E^c	K^d
R	R′		H-ZSM-5-70-C_{18}	H-ZSM-5-70		
CH_3	CH_3	6.2	21.3	21.8	0.98	3.3 ± 0.2
CH_3	C_2H_5	5.1	13.7	12.7	1.08	8.8 ± 0.2
CH_3	C_3H_7	2.5	79.3	66.1	1.20	26 ± 3
CH_3	$C_4H_9^e$	3.1	5.45	5.50	0.991	3.5 ± 0.7[e]
CH_3	C_6H_{13}	2.5	9.99	5.07	1.97	16 ± 3
CH_3	C_7H_{15}	2.5	33.1	3.60	9.19	82 ± 3
CH_3	C_8H_{17}	2.5	5.62	0.36	15.6	(3.1 ± 0.2) × 10^5
CH_3	$C_{12}H_{25}$	2.5	5.44	0.090	60.4	(4.7 ± 0.1) × 10^8
CH_3	CH_2Ph	2.5	1.79	0.728	2.45	83 ± 2
C_2H_5	C_3H_7	2.5	23.6	23.3	1.01	1.4 ± 0.3
C_3H_7	C_4H_9	2.5	30.7	2.48	12.4	250 ± 40
Ph	C_2H_5	2.5	1.27	0.522	2.44	131 ± 8
C_5H_{11}	CH_3	2.5	17.5	7.92	2.21	110 ± 17
C_5H_{11}	C_2H_5	2.5	12.2	4.98	2.45	191 ± 2
C_9H_{19}	CH_3	2.5	7.05	1.74	4.05	77 ± 4
C_9H_{19}	C_2H_5	2.1	3.30	0.775	4.23	120 ± 5

[a] Conditions are as in the main text. No reaction was observed without any catalyst.
[b] Initial rate of hydrolysis.
[c] $E = R_i$ (H-ZSM-5-70-C_{18})/R_i (H-ZSM-5-70).
[d] Partition coefficients of esters $K = C$(toluene)/C(water) at 25°C.
[e] Hexane-water solvent system.

results of H-ZSM-5-70-C_{18} catalytic hydrolysis of various esters are summarized in Table 5. Partition coefficients of the esters measured in toluene-water solvent system are also listed. For relatively water-insoluble esters such as dodecyl acetate, octyl acetate, and butyl butyrate, the rates of hydrolysis increased by octadecyltrichlorosilane treatment of H-ZSM-5-70. For the fairly water-soluble esters such as methyl acetate, ethyl acetate, butyl acetate, and propyl propionate, the rates did not increase using the treated catalyst. The most pronounced effect of the treatment was found in the case of dodecyl acetate when the rate increased by ca. 60 times.

The high efficiency of octadecyltrichlorosilane treatment of H-ZSM-5-70 for the hydrolysis of water-insoluble

TABLE 6

Silylation Effect on the Hydrolysis[a]

Ester	Zeolite	Silylating reagent	R_i^b (10^{-4} mol g^{-1} h^{-1})
Octyl acetate	None	None	0.00[c]
Octyl acetate	H-ZSM-5-70	None	0.41
Octyl acetate	H-ZSM-5-70-$C_6H_5(E_tO)$	$C_6H_5Si(OC_2H_5)_3$	0.56
Octyl acetate	H-ZSM-5-70-$(C_6H_5)_3(E_tO)$	$(C_6H_5)_3SiOC_2H_5$	0.37
Octyl acetate	H-ZSM-5-70-$C_8(E_tO)$	$C_8H_{17}Si(OC_2H_5)_3$	0.62
Octyl acetate	H-ZSM-5-70-$C_{18}(E_tO)$	$C_{18}H_{37}Si(OC_2H_5)_3$	0.62
Octyl acetate	H-ZSM-5-70-C_{18}	$C_{18}H_{37}SiCl_3$	4.32
Octyl acetate	H-ZSM-5-70-$(C_1)_2$	$(CH_3)_2SiCl_2$	2.43
Benzyl acetate	None	None	1.39[c]
Benzyl acetate	H-ZSM-5-70	None	2.71
Benzyl acetate	H-ZSM-5-70-$C_6H_5(E_tO)$	$C_6H_5Si(OC_2H_5)_3$	1.55
Benzyl acetate	H-ZSM-5-70-(C_6H_5)	$C_6H_5SiCl_3$	23.83
Benzyl acetate	H-ZSM-5-70-C_{18}	$C_{18}H_{37}SiCl_3$	2.23

[a] Octyl acetate (0.13 mmol: 22.4 mg) or benzyl acetate (3.5 mmol: 520 mg) and zeolite (40 mg) were used. Other conditions are as in the text.
[b] Initial rate of hydrolysis.
[c] The assumption that 40 mg of the zeolite would be used.

TABLE 7

Dependence of the Hydrolysis of Octadecyl Acetate Catalyzed by H–ZSM-5-70–C_{18} on pH[a]

Additives	pH	R_i[b] (10^{-4} mol g^{-1} h^{-1})
None	6.6	0.00[c]
None	6.6	5.62
HCl	6.3	5.74
HCl	3.6	5.34
HCl	2.4	5.61
HCl	1.2	5.60
H_2SO_4	1.4	5.42
NaOH	8.8	0.11

[a] Octyl acetate (2.5 mmol: 429 mg) and H–ZSM-5-70–C_{18} (40 mg) were used. Other conditions are as in the main text.

[b] Initial rate of hydrolysis.

[c] Absence of H–ZSM-5-70–C_{18}, and the assumption that 40 mg of the zeolite would be used.

esters was caused presumably by the increase of interactions between H–ZSM-5-70 catalyst and the esters. Thus, the H–ZSM-5-70–C_{18} performed a new type of interface catalysis.

Effect of Silylating Reagent

Alkyl modified H–ZSM-5-70s prepared with various kinds of silylating reagents were tested for the hydrolysis of octyl acetate and benzyl acetate. The rates of hydrolysis are listed in Table 6. Octadecyltrichlorosilane was the most effective reagent for the hydrolysis. On the other hand, phenyltrichlorosilane was the most effective treatment for the hydrolysis of benzyl acetate. These facts suggest that the reagent with a similar molecular structure to the substrate ester is effective. Table 6 also shows that chlorosilane reagents are more effective than the corresponding ethoxide reagents. The influence of the Cl^- anion, which was produced upon the preparation of the alkylated zeolites, on the activity of the catalyst will be discussed in the following sections.

Dependence of the Activity on pH

Dependence of the activity of catalyst on pH of water phase was examined (Table 7). The hydrolysis by H–ZSM-5–C_{18} proceeded regardless of the pH range between 1.2–6.6 of the water layer and regardless of the species of the counter anion. No reaction occurred in the absence of the catalyst. These findings clearly show that the reaction occurred at the acid sites of the H–ZSM-5-70, but not in the solution. When the pH value was set at 8.8, the reaction was suppressed. H–ZSM-5-70–C_{18} in water at pH 8.8 had only very weak acid sites ($+4.8 < \mathrm{Ho} \leq +6.8$) (see Table 8). It seems that most of the acid sites were neutralized and the reaction was retarded.

As described under "Effect of Silylating Reagent," the chlorosilane reagents afforded more effective catalyst than the corresponding ethoxide reagents. The Cl^- anion produced in the course of the preparation of alkylated zeolites might be responsible for the activity of the catalyst. However, the addition of Cl^- anion to the water in the pH range 1.2–6.6 did not affect the activity of the catalyst. Chen reported the preparation of the high-silica mordenite by dealumination treating with H_2O and HCl (10). In this study, dealumination of H–ZSM-5-70 also might have occurred by released HCl during the prepara-

TABLE 8

Acid Strength of Various Types of Zeolite–C_{18}[a] and SiO_2–Al_2O_3–C_{18}[a] in Water

Catalyst	Si/Al[b]	Ho						
		+6.8	+4.8	+3.3	+1.5	−3.0	−5.6	−8.2
H–ZSM-5-70	39.0	+	+	+	+	+	−	−
H–ZSM-5-70–C_{18}	39.0	+	+	+	+	+	−	−
H–ZSM-5-70–C_{18}[c]	39.0	+	−	−	−	−	−	−
H–Z-HM20	10.1	+	+	+	+	±	−	−
H–Z-HM20–C_{18}	10.1	+	+	+	+	*	*	*
H–Z-HM15	7.5	+	+	+	+	±	−	−
H–Z-HM15–C_{18}	7.5	+	+	+	+	*	*	*
H–Z-Y4.8	2.1	+	+	+	+	−	−	−
H–Z-Y4.8–C_{18}	2.1	+	+	+	+	−	−	−
SiO_2–Al_2O_3	5.3	+	+	+	−	−	−	−
SiO_2–Al_2O_3–C_{18}	5.3	+	+	+	−	−	−	−

Note. +, Acidic color; ±, slightly acidic color; −, basic color; *, too ambiguous to be judged.

[a] The catalysts were prepared by treating with octadecyltrichlorosilane.

[b] The Si/Al ratios of zeolites were calculated on the basis of the SiO_2 and Al_2O_3 contents.

[c] The pH was adjusted to 8.8 by addition of 1.0 mol liter^{-1} NaOH aqueous solution.

TABLE 9

Shape-Selective Property for the Hydrolysis of Esters over H–ZSM-5–C_{18}[a]

RC(=O)OR′		H–ZSM-5-70–C_{18}		SiO_2–Al_2O_3–C_{18}		Shape-selective property (k'/k'')
R	R′	R_i[b] (10^{-4} mol g^{-1} h^{-1})	k'[c]	R_i[b] (10^{-4} mol g^{-1} h^{-1})	k''[c]	
CH_3	CH_3	86.60	1	20.15	1	1
C_5H_{11}	CH_3	17.51	0.20	7.13	0.35	0.57
C_5H_{11}	C_2H_5	12.22	0.14	6.16	0.31	0.45
CH_3	C_8H_{17}	5.62	0.06	4.78	0.24	0.25
C_9H_{19}	CH_3	7.05	0.08	5.49	0.27	0.30
C_9H_{19}	C_2H_5	3.30	0.04	4.91	0.24	0.17

[a] H–ZSM-5-70–C_{18} or SiO_2–Al_2O_3–C_{18} (40 mg) and esters (2.5 mmol) were used. Other conditions are as in the main text.

[b] Initial rate of hydrolysis.

[c] Relative rates.

tion of H–ZSM-5-70–C_{18} by use of octadecyltrichlorosilane reagent.

Acid Strength

The determinations of the acid strength of the zeolite catalysts were carried out in water by use of Hammett indicators, and the results are summarized in Table 8. Intrinsic acid strength of zeolites and SiO_2–Al_2O_3 was maintained even after the treatment with octadecyltrichlorosilane. H–ZSM-5-70–C_{18} has the strongest value ($-5.6 < Ho \leq -3.0$), and SiO_2–Al_2O_3–C_{18} has the weakest value ($+1.5 < Ho \leq +3.3$).

H–ZSM-5-70–C_{18} shows the highest activity for the hydrolysis, and zeolites having the higher acidity show the higher activities as shown in Table 3.

The pore openings of zeolites are not sterically rigid. Recent papers reveal that substrates, which are significantly larger in size than the pore openings of the zeolites, enter the pores, for example, formation of cyclophane in the Na–X-type zeolite and encapsulation by a ship in bottle through the diffusion of bi-radical produced from 12-membered phenylcyclanone (*11*), photolysis of dibenzyl ketone in the X-type and Y-type zeolites (12), photorearrangement of α-alkyldeoxybenzoines in Li–X and Li–Y zeolites (13), photochlorination of *n*-alkane C_n (n = 12, 13, 18, and 20) in pentasyl zeolite (14), and dynamic behavior of *o*-, *m*-, *p*-xylene in ZSM-5 by computer calculation (15). Most Hammett indicators may be capable of diffusion into the pore of zeolites. The observed correlation between the acid strength by this method and the activity of the zeolite can be rationalized as reflective of contributions from the diffusion of the indicators. However, it is not exactly ascertained what degree of acid strength of acid sites at the internal and/or external surface affects the reaction.

As mentioned above, H–ZSM-5-70–C_{18} catalyst treated with the chlorinated reagents showed higher activity than those treated with the ethoxide reagents. However, intrinsic acid strength of H–ZSM-5-70 was maintained even after the preparation by chlorinated reagents. The dealumination of H–ZSM-5 as mentioned above might increase the number of the acid sites, but not the acid strength.

Shape-Selective Property

The shape-selective property of H–ZSM-5-70–C_{18} was examined in the hydrolysis of esters with straight chain. Results over H–ZSM-5-70–C_{18} together with SiO_2–Al_2O_3–C_{18} are summarized in Table 9. It shows that H–ZSM-5-70–C_{18} was more active than SiO_2–Al_2O_3–C_{18}. Activities of both catalysts become lower with an increase in the total carbon number of the esters. The value k'/k'' also becomes lower with an increase in a total carbon number of the esters. The lowest value 0.17 was found in the case of ethyl decanoate, where H–ZSM-5-70–C_{18} showed lower activity than SiO_2–Al_2O_3–C_{18}.

The overall reaction rate would depend on the diffusion of the esters to the surface of the H–ZSM-5-70–C_{18}. The ester with long chain is hard to diffuse to the surface of the zeolite. This would lead to a retardation of the reaction rate, and the effect of shape-selective property of the zeolite becomes significant. Then the value k'/k'' would reflect shape-selective property of H–ZSM-5-70–C_{18}, taking into account the little shape-selective property of SiO_2–Al_2O_3. Empirically, the shape-selective photolysis of dibenzyl ketone over SiO_2 has been reported to be poor (16, 17). Thus, the shape-selective property of H–ZSM-5 was maintained after the treatment with alkyl–silane reagent.

CONCLUSIONS

Treatment of H–ZSM-5 with octadecyltrichlorosilane permitted the treated catalyst to concentrate at the toluene–water interface where it can catalyze the hydrolysis of organic soluble esters. Hence H–ZSM-5 obtained lipophylicity and incorporated organic molecules. Intrinsically strong acid sites of H–ZSM-5 were maintained during the treatment. Therefore, octadecyltrichlorosilane-treated H–ZSM-5 could perform a new type of catalysis for the hydrolysis of water-insoluble esters accompanying shape-selective properties.

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