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Catalysis at the toluene / water interface: shape-selective hydrolysis of esters having some rings and lactones promoted by octadecyl immobilized H-ZSM-5 catalyst

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Shape-selective properties of octadecyltrichlorosilane-treated H-ZSM-5, abbreviated as H-ZSM-5–C_{18}, have been observed in the hydrolysis of esters having some rings and lactones in toluene–water solvent system. The shape-selectivity for the reaction has been evaluated by the ratio $k'_{HCl}/k'_{H\text{-}ZSM\text{-}5\text{-}C_{18}}$ of the relative rate constants in comparison with the rate constant of methyl acetate. The selectivity became higher with increase in bulkiness of the substrate. Substrates having the minimum diameter larger than 6.5 Å, significantly larger in size than the pore openings of ZSM-5, could not react in this system.

Keywords: H-ZSM-5–C_{18}; shape-selectivity; hydrolysis of esters

1. Introduction

Zeolites draw much attention because of the remarkable characteristic of shape-selective property upon homogeneous crystalline structures besides acid–base property. Hence, zeolites have been used for organic syntheses [1], where the substrate molecules react in the cavity or channel with suppression of translational movement. Examples of shape-selective reactions 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]. The key for the selectivity in organic reactions is unequivocally attributed to the pores of the zeolites.

Statistic diameters of pores of zeolites and sizes of molecules locating inside the pores are not always a definite guide to the actual possibility of molecular diffusion inside the pore. Examples are shown in the case of selective alkylation of toluene with methanol [7] and isomerization of alkylanilines [8] on H-ZSM-5. In practice, not only *p*-xylene but also *o*- and *m*-xylene can diffuse inside the pore. A recent study of simulation of dynamic behaviors of molecules inside the pores of ZSM-5 using a super minicomputer has reported that benzene, toluene, and xylene isomers are excited and can pass through the pores of the zeolite [9].

Niwa et al. have used the chemical vapor deposition of silicon alkoxides onto zeolites for controlling the pore-opening size, inactivation of the external surface, and solid acidity. By use of that method, a thin silica layer has been obtained on the external surface of zeolites; the deposited silica controls the pore-opening size [10]. We have been interested in the application of zeolites to organic reactions in the liquid phase and have reported that octadecyl-silane-treated H-ZSM-5, abbreviated as H-ZSM-5–C_{18}, showed a new type of interface catalysis, where the shape-selective hydrolysis of esters [11] and hydration of epoxides [12] was observed. In these reactions dynamic behaviors of substrate molecules inside the pores of ZSM-5 are reflected in catalysis, where the overall reaction rate will be influenced by diffusion of the molecules in the pores of the zeolite. It is not clear whether the certain evidence of the shape-selectivity has been obtained because of the use of aliphatic compounds with chains as substrates which appear to be capable to moderately easily diffuse into the pores of the zeolite. This paper reports the evidence of the shape-selectivity in hydrolysis by use of esters having variation in size (eq. (1)):

$$\mathrm{RCOOR'} + \mathrm{H_2O} \xrightarrow[\text{toluene/H}_2\text{O}]{\text{H-ZSM-5–C}_{18}} \mathrm{RCOOH} + \mathrm{R'OH} \qquad (1)$$

2. Experimental

2.1. Catalyst preparation

H-type zeolite H-ZSM-5 was prepared from ZSM-5-70Na (Mobil Oil Co., distributed as "standard" catalyst sample) by a conventional cation exchange procedure using 1 mol ℓ^{-1} NH_4Cl aqueous solution followed by calcination in air at 500°C.

An octadecyl immobilized H-ZSM-5 (abbreviated as H-ZSM-5–C_{18}) was prepared by treating H-ZSM-5 with octadecyltrichlorosilane [13]. One molecule of the octadecylsilyl group was attached per unit cell of the zeolite [11].

2.2. *Procedure of hydrolysis and analysis*

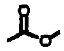
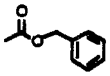
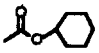
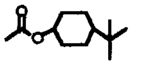
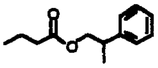
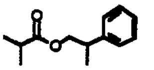
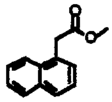
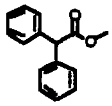
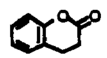
A typical example of the hydrolysis of ester is illustrative. H-ZSM-5–C_{18} (40 mg) and cyclohexyl acetate (2.5 mmol, 356 mg) were added to a mixture of toluene (5.0 ml) and distilled water (5.0 ml) in a 50 ml flask, and the suspension was refluxed.

Aliquots of the reaction mixture 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 the authentic samples.

3. Results and discussion

H-ZSM-5–C_{18} catalyst readily promoted the hydrolysis of the esters having rings and lactones. The reaction rates were measured, and first-order rate constants (k) in the substrates are listed in table 1. Relative rate constants (k') were estimated in comparison with the rate constant of methyl acetate taking into account fairly easy diffusion into the pore of zeolite. Relative rate constants k' in a HCl solution are also listed. The substrates having smaller size showed large values of k and the substrates having the minimum diameter larger than 6.5 Å could not react in this system, while the substrates in a

Table 1
Shape-selective hydrolysis of esters and lactones over H-ZSM-5–C_{18} [a]

Substrate	Structure	Diameter [b]	H-ZSM-5–C_{18}		HCl k' [e]	S [c]
			k [d]	k' [e]		
methyl acetate		5.3	27.25	1	1 [f]	1
benzyl acetate		6.3	0.658	0.024	0.393	16.3
cyclohexyl acetate		6.4	0.0379	0.001	0.296	212
methyl phenylacetate		6.5	0.000	0.000	0.312	∞
4-*t*-butylcyclohexyl acetate		7.2	0.000	0.000	0.653	∞
2-phenylpropyl butyrate		7.9	0.000	0.000	0.260	∞
2-phenylpropyl isobutyrate		7.9	0.000	0.000	0.403	∞
methyl 1-naphthaleneacetate		8.6	0.000	0.000	0.008	∞
methyl diphenylacetate		9.6	0.000	0.000	0.067	∞
ε-caprolactone		5.8	406.1	14.97	28.08	1.88
1,2-dihydrocoumarin		6.2	1.085	0.040	1.184	29.6

[a] H-ZSM-5–C_{18} (40 mg) or HCl (0.82 mmol) were added to a mixture of toluene (5.0 ml) and water (5.0 ml), and the suspension was refluxed.
[b] Minimum diameters of the substrate molecules were estimated by space filling model.
[c] Shape-selectivity $S = k'_{\mathrm{HCl}}/k'_{\mathrm{H\text{-}ZSM\text{-}5\text{-}C_{18}}}$.
[d] First-order rate constants in the esters or lactones: $k/10^{-1}$ g-cat^{-1} h^{-1}.
[e] Relative rate constants.
[f] First-order rate constant equals 1.462×10^{-1} h^{-1}.

Table 2
Shape-selectivities over H-ZSM-5–C_{18} and H-ZSM-5 [a]

Substrate	S^b	
	H-ZSM-5–C_{18}	H-ZSM-5
methyl acetate	1	1
benzyl acetate	16.3	15.1
cyclohexyl acetate	212	223
methyl phenylacetate	∞	∞
4-*t*-butylcyclohexyl acetate	∞	∞
2-phenylpropyl butyrate	∞	∞
2-phenylpropyl isobutyrate	∞	∞
methyl 1-naphthaleneacetate	∞	∞
methyl diphenylacetate	∞	∞
ε-caprolactone	1.88	1.77
1,2-dihydrocoumarin	29.6	28.1

[a] Reaction conditions are as in table 1.
[b] Shape-selectivity $S = k'_{\mathrm{HCl}}/k'_{\mathrm{zeolite}}$ defined as in table 1.

HCl solution showed reactivities to a certain extent. Lactones were inclined to show higher reactivities than esters.

The shape-selective property of H-ZSM-5–C_{18} in catalysis has been evaluated by comparing the reaction rates over H-ZSM-5–C_{18} with those in HCl solution. Shape-selectivity over H-ZSM-5–C_{18} catalyst can be estimated by the ratio $k'_{\mathrm{HCl}}/k'_{\mathrm{H\text{-}ZSM\text{-}5\text{-}C_{18}}}$ of relative rate constants in comparison with the rate constant of methyl acetate, taking into account the non-shape-selective property of the HCl catalyst. The value would be ascribed primarily to the size of the substrate. The shape-selectivity becomes higher with increase in the diameter of the substrate. The most pronounced value except infinity was found in the case of cyclohexyl acetate (the minimum diameter: 6.4 Å), viz. ca. 212. The substrates having the diameter larger than 6.5 Å, significantly larger in size than the pore openings of ZSM-5, could not react in this system. These results clearly indicate that the substrates being significantly larger in size than the pore openings of ZSM-5 could not diffuse into the pore of the zeolite in this system. Similar values of the selectivities were also observed over naked H-ZSM-5 catalyst in this reaction (table 2). This implies that the pore of the zeolite was maintained with intrinsic character in size after the preparation of the octadecyl immobilized H-ZSM-5 by the treatment with octadecyltrichlorosilane.

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