Influence of solvents on hydration of 1,2-epoxyhexane over H-ZSM-5–C_{18} catalyst

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The influence of solvents such as benzene, toluene, *m*-xylene, and neighbours on the hydration of 1,2-epoxyhexane caused by the pore of H-ZSM-5–C_{18} catalyst was studied by measurement of the reaction rate. The largest retardation of the hydration was observed using *m*-xylene as solvent. Any other solvents did not show so large a retardation as that of *m*-xylene. By taking advantage of the retardation with *m*-xylene the effect of the pores of various types of zeolites on the rate could be dynamically demonstrated.

Keywords: ZSM-5; hydration of epoxide; solvent effect; shape-selective property; pore size

1. Introduction

Inorganic porous solids such as zeolite and clay are attracting much attention of organic chemists because of remarkable characteristics of shape-selective properties besides acid–base properties [1]. Zeolites have homogeneous crystalline structures, and hence shape-selective reactions using them were achieved and reported. Examples of recent works are 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 to the selectivity of reactions is unequivocally attributed to the pore size of the zeolites.

In the cases of selective alkylation of toluene with methanol [7] and isomeriza-

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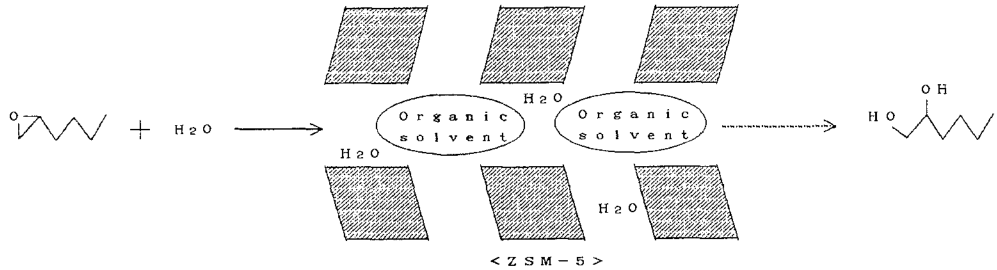
tion of alkylanilines [8] on H-ZSM-5, statistic diameters of pores of zeolites and sizes of molecules inside the pores are not a definite guide to the actual possibility of molecular diffusion inside the pore. In practice, not only *p*-xylene but also *o*- and *m*-xylene can diffuse inside the pore; furthermore, smaller dimethylaniline isomers can diffuse, but larger dimethylaniline isomers can not, in spite of statistically larger diameters of these molecules than that of the pore of zeolite. A recent study of simulation of dynamic behaviors of benzene, toluene, and xylene isomers inside the pores of ZSM-5 using a super minicomputer has reported that molecules are excited and can pass through the pores of ZSM-5. The interaction between methyl groups of xylene isomers, except *p*-xylene, and the pore wall of ZSM-5 was shown to be larger than that of others by the calculation of their energy levels inside the ZSM-5 pore [9].

We have reported that alkyl-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 esters [10] and shape-selective ring-openings of epoxides [11] were observed. In these reactions dynamic behaviors of molecules inside the pore are reflected in catalysis, where the overall reaction rate will be influenced by diffusion of the molecules in the pore of the zeolite. When bulky solvents are in the pore of the zeolite, a tight fit between the zeolite host and the guest molecules is brought about, and the reaction rate will be retarded. This paper reports the influence of solvents on hydration of 1,2-epoxyhexane through the retardation of the rate caused primarily by the size of the solvent molecule (scheme 1).

2. Experimental

Hydration of 1,2-epoxyhexane by zeolites–C_{18} and SiO_2–Al_2O_3–C_{18} was attempted. Zeolites–C_{18} (40 mg) or SiO_2–Al_2O_3–C_{18} (40 mg) and epoxides (13.0 mmol) were added to an organic solvent (5.0 ml) and water (5.0 ml) mixture, and the suspension was refluxed. Both zeolites–C_{18} and SiO_2–Al_2O_3–C_{18} catalysts floated on the organic solvent–water interface, while the non-alkylated H-ZSM-5 was in suspension in the water. The reaction occurred quantitatively to produce diols. No reaction other than ring-opening was observed.



Scheme 1.

Zeolites–C_{18} were prepared by treating zeolites with octadecyltrichlorosilane [12] after a conventional cation exchange using 1 N NH_4Cl aq. solution and calcination of zeolites (a "standard" ZSM-5 sample of Mobil Oil Co., "standard" catalyst samples of the Catalysis Society of Japan, and Wako Chemicals). SiO_2–Al_2O_3–C_{18} was also prepared by treating SiO_2–Al_2O_3 (a "standard" catalyst sample of the Catalysis Society of Japan (JRC-SAL-2; 13.8% alumina)) with octadecyltrichlorosilane.

3. Results and discussion

Organic solvents such as benzene, toluene, *m*-xylene, and neighbors, some of which are expected to fit tightly as a guest molecule in a pore of zeolite, were chosen for hydration of 1,2-epoxyhexane. Results are summarized in table 1. The reaction rates over H-ZSM-5-25H–C_{18} and H_2SO_4 catalysts were measured in order to compare the rates in the solvents used. The ratio of relative rate constants, k'/k'', denotes the relative magnitude of reaction rate using a certain organic solvent, based on the rate in toluene solvent. A smaller value of the ratio means a larger retardation of the rate. Factors for causing retardation, such as boiling point and permittivity, appear to be negligible taking into account the comparison with the rate using H_2SO_4 as the catalyst. The value would be ascribed primarily to the size of the solvent molecule. The largest retardation was observed in the reaction using *m*-xylene. Any other solvents did not show so large a retardation as *m*-xylene. The largest tight fit of *m*-xylene in the ZSM-5 pore might cause the largest retardation of the rate as Inui et al. have calculated in ref. [9]. It is not clearly interpreted that the value of k'/k'' in toluene showed so relatively high.

Hydration of 1,2-epoxyhexane over various types of zeolites with specific pore size as a catalyst were studied using *m*-xylene and toluene as organic solvents. Results are summarized in table 2. The largest retardation in *m*-xylene was

Table 1
Influence of organic solvents on the hydration of 1,2-epoxyhexane[a]

Organic solvent	bp (°C)	H-ZSM-5-25H–C_{18}		H_2SO_4[b]		k'/k''
		k^c	k'^d	k^c	k''^d	
toluene	111	31.8	1	37.9	1	1
benzene	80	2.1	0.066	8.8	0.23	0.29
m-xylene	138–9	3.9	0.12	67.1	1.77	0.068
cyclohexane	81	7.3	0.23	20.0	0.53	0.43
n-hexane	69	3.7	0.12	22.2	0.59	0.20

[a] 1,2-epoxyhexane (13.0 mmol: 1300 mg) and H-ZSM-5-25H–C_{18} (40 mg) were used. Other conditions as in the main text.

[b] H_2SO_4 (0.15 mmol) was added in the reaction system (pH 1.0–1.2 in water phase).

[c] First-order rate constants in epoxides (10^{-2} g^{-1} cat h^{-1}).

[d] Relative rate constants.

Table 2
Hydration of 1,2-epoxyhexane over various types of zeolite catalysts[a]

Catalyst[b] (type)	*m*-xylene		Toluene		k''/k'
	k[c]	k'[d]	k[c]	k''[d]	
H_2SO_4[e]	67.1	1	37.9	1	1
H-F-9–C_{18}[f] (faujasite)	9.0	0.13	12.0	0.32	2.4
H-Z-Y5.6–C_{18} (Y)	18.2	0.27	20.8	0.55	2.0
H-Z-HM15–C_{18} (mordenite)	7.5	0.37	32.6	0.86	2.3
H-ZSM-5-25H–C_{18}	12.3	0.059	31.8	0.84	14.3
H-ZSM-5-25H	12.3	0.044	25.8	0.68	15.3
SiO_2–Al_2O_3–C_{18}[g]	5.3	0.064	10.9	0.29	4.5

[a] Conditions as in the main text.
[b] Catalyst–C_{18} represents the catalyst treated with octadecyltrichlorosilane.
[c] First-order rate constants in the epoxides 10^{-2} g^{-1} cat h^{-1}.
[d] Relative rate constants.
[e] H_2SO_4 (0.15 mmol) was added in the reaction system (pH 1.0–1.2 in water phase).
[f] Wako Chemicals.
[g] 13.8% Al_2O_3.

observed in the former experiment (table 1), based on the rate in toluene. The ratio of relative rate constants, k''/k', would be affected by the influence of the pore size of the zeolites on the hydration. A larger value implies a larger contribution of the zeolite pore to the rate retardation attributed to pore size. The largest value, 15.3, was observed in the reaction over H-ZSM-5-25H. Values over other zeolites which have larger pore sizes than H-ZSM-5 were equal to about 2. A similar value to that over H-ZSM-5-25H was obtained over H-ZSM-5-25H–C_{18}. This similarity suggests that the pore was maintained geometrically as it was, even after pretreatment of H-ZSM-5 with octadecyltrichlorosilane. The fact that H-ZSM-5–C_{18} maintains the same acid strength in water as that of H-ZSM-5 supports this [13]. Interestingly, for SiO_2–Al_2O_3–C_{18} the value was intermediate between those of H-ZSM-5 and other zeolites. This presumably reflected the existence of the pore size distribution as a cause of the retardation of the rate.

The effect of the pores of zeolites on the rate could be dynamically demonstrated by taking advantage of the retardation with *m*-xylene as a solvent in the hydration of 1,2-epoxyhexane.

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