Octadecyl immobilized H-ZSM-5-catalyzed ring-openings of epoxides with water in liquid phase accompanying shape-selective property

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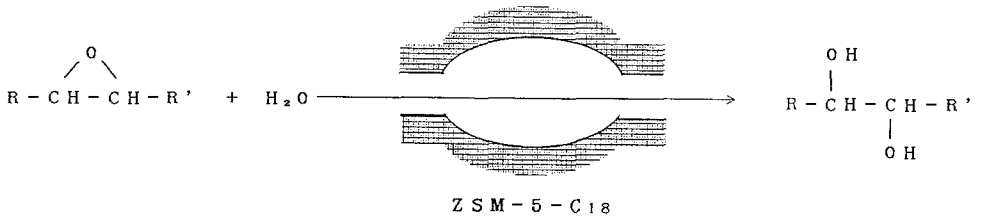
The octadecyltrichlorosilane-treated ZSM-5 catalyst H-ZSM-5–C_{18} exhibited high activity in the ring-opening reaction of epoxides in a toluene–water solvent. The shape-selective property of H-ZSM-5–C_{18} in the liquid phase has also been observed by comparing the reaction rates with those over octadecyltrichlorosilane treated SiO_2–Al_2O_3.

Keywords: ZSM-5; alkylsilane treatment; shape-selective property; ring-opening reaction; epoxide

1. Introduction

Highly selective reactions have been achieved by use of inorganic porous solids in which the substrate molecules orientate in the cavity or channels with suppression of their translational movement [1]. Zeolites are attracting much attention of organic chemists because they exhibit remarkable shape-selective properties besides the acid–base properties due to homogeneous crystalline structures. Examples of recent reports using zeolites in organic syntheses are the photolysis of alkanophenones [2] and dibenzyl ketone [3], ring-opening reactions of 2,3-epoxy alcohols [4], alkylation of toluene [5], and isomerization of meta-xylene [6].

We have reported that the alkylsilane-treated ZSM-5 catalyst showed a new type of interface catalysis, where an acceleration of the hydrolysis of esters was observed [7]. This paper reports the application of the catalyst to ring-opening



Scheme 1.

reactions of epoxides in the liquid–liquid phase. The application will make the separation of the products easy in addition to the easy separation of catalyst, i.e. the water-insoluble epoxides are converted to water-soluble diols. This method could improve the procedure of the ring-opening of epoxides. Further, we find indeed that the catalyst shows a shape-selective property in this reaction system besides its capacity of accelerating the reaction (scheme 1).

2. Experimental

H-ZSM-5-25H–C_{18} was prepared by treating H-ZSM-5-25H with octadecyltrichlorosilane [8] after a convential cation exchange and calcination of ZSM-5-25H (a "standard" ZSM-5 sample of Mobil Oil Co.) using a 1 N NH_4Cl aqueous solution. 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. Ring-opening reactions of epoxides by H-ZSM-5-25H–C_{18} and SiO_2–Al_2O_3–C_{18} were attempted. H-ZSM-5-25H–C_{18} or SiO_2–Al_2O_3–C_{18} (40 mg) and epoxides (13.0 mmol) were added to a mixture of toluene (5.0 ml) and water (5.0 ml), and the suspension was refluxed. Both H-ZSM-5-25H–C_{18} and SiO_2–Al_2O_3–C_{18} catalysts floated on the toluene–water interface, while the non-alkylated H-ZSM-5 was suspended in the water. The reaction occurred quantitatively to produce diols. No reaction other than the ring-opening was observed.

3. Results and discussion

Various types of zeolites were studied as catalyst for the ring-opening reaction of 1,2-epoxyhexane and the results are summarized in table 1. Table 1 shows that the H-Z-HM15–C_{18} and H-ZSM-5–C_{18} catelysts exhibited higher activity. These zeolites have higher Si/Al atomic ratios. In all types of zeolites the ratios affect the acid strength, and the higher the ratio the stronger the acid sites, even in amorphous SiO_2–Al_2O_3 [9]. Acid sites or acid sites in combination with base sites of the zeolite presumably promoted the reaction. A higher

Table 1
The ring-opening of 1,2-epoxyhexane under various zeolites [a]

Zeolite [b] (type)	Si/Al atomic ratio	k [c] (10^{-2} g^{-1} cat h^{-1})
H-A-C_{18} (4A type)	1.0	4.8
H-F-C_{18} (faujasite type)	1.3	12.0
H-Z-Y5.6-C_{18} (Y type)	2.8	20.8
H-Z-HM15-C_{18} (mordenite type)	7.5	32.6
H-ZSM-5-25H-C_{18}	12.3	31.8 (17.0) [d]
H-ZSM-5-25H	12.3	25.8
SiO_2-Al_2O_3-C_{18} [e]	5.3	10.9

[a] 1,2-epoxyhexane (13.0 mmol: 1300 mg) and zeolite (40 mg) were used. Other conditions as in the main text.
[b] Zeolite-C_{18} represents the zeolite treated with octadecyltrichlorosilane.
[c] First-order rate constants in the epoxides.
[d] Acetone (5.0 ml)–water (5.0 ml) solvent system.
[e] 13.8% Al_2O_3.

reaction rate was observed in the reaction using H-ZSM-5-25H-C_{18} comparing with the use of non-alkylsilane-treated H-ZSM-5-25H. Interestingly, the rate in the toluene–water solvent is higher than that in an acetone–water solvent.

Results for aliphatic and alicyclic epoxides over H-ZSM-5-25H-C_{18} and SiO_2-Al_2O_3-C_{18} are summarized in table 2. The rate constants in various epoxides over H-ZSM-5-25H-C_{18} are higher than those over SiO_2-Al_2O_3-C_{18} except in the case of epoxycyclododecane. The shape-selectivity property of

Table 2
Shape-selective ring-openings of epoxides over H-ZSM-5-C_{18} catalyst [a]

R-CH(O)CH-R′		H-ZSM-5-25H-C_{18}		SiO_2-Al_2O_3-C_{18} [b]		Shape-selective property k''/k'
		k [c] (10^{-2} g^{-1} cat h^{-1})	k' [d]	k [c] (10^{-2} g^{-1} cat h^{-1})	k'' [d]	
CH_3	H	1160.0	1	420.0	1	1
C_2H_5	H	480.0	0.41	253.0	0.60	1.5
C_4H_9	H	31.8	0.027	10.9	0.026	1.0
C_6H_{13}	H	7.8	0.0067	6.9	0.016	2.4
Ph	H	1510.0	1.30	210.0	5.15	4.0
$-(CH_2)_3-$		778.0	0.67	268.0	0.64	1.0
$-(CH_2)_4-$		1070.0	0.99	623.0	1.49	1.5
$-(CH_2)_6-$		1.6	0.0014	1.0	0.0023	1.6
$-(CH_2)_{10}-$		0.0	0.0	0.7	0.0016	∞

[a] Conditions as in the text.
[b] 13.8% Al_2O_3.
[c] First-order rate constants in epoxides.
[d] Relative rate constants.

H-ZSM-5-25H–C_{18} can be evaluated by the ratio of the relative rate constants k''/k' taking into account the slightly shape-selective property of the SiO_2–Al_2O_3 surface in organic reactions in comparison with that of zeolites. The shape-selective photolysis of dibenzyl ketone over SiO_2 has been reported to be poor [10,11]. The shape-selective property was inclined to increase with increasing total carbon number of the epoxides. This pronounced effect was found in the case of epoxycyclododecane and styrene oxide, i.e. ∞ and about 4 times, respectively. In the reaction of epoxycyclododecane, the epoxide could hardly immerse in the cavity of ZSM-5, therefore no reaction occurred. Thus, the alkylsilane-treated ZSM-5 catalyst shows shape-selective property in the liquid phase besides its capacity of accelerating the ring-openings of epoxides.

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