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Acylation of amines by aminolysis of esters over H-ZSM-5 catalyst

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Abstract

H-ZSM-5 of zeolite resulted in an effective catalyst for the acylation of amines by aminolysis of esters such as octyl acetate. The shape-selective properties of the catalyst were investigated in the reaction between some amines and octyl acetate. H-ZSM-5 also performed some nucleophilic reactions such as hydrolysis and alcoholysis of esters. (in Japanese)

Key words: H-ZSM-5 of zeolite, acylation of amines, aminolysis, shape-selective property

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1. Introduction

Chemical processes using liquid acids such as sulfuric acid, hydrofluoric acid, and aluminum chloride present disposal or toxicity problems. In place of the processes, clean chemical processes using solid acids are desirable¹. The application of solid acids further makes separation process easy. Among solid acids, environmentally friendly oxide-based solid acids are required², but they generally lose their activities in water due to poisoning of water.

Zeolites draw much attention because of the remarkable characteristic of shape selective property upon homogeneous crystalline structures besides acid-base property³, where the substrate molecules react in the cavity or channel with suppression of translational movement. Hence, zeolites have been used for organic syntheses⁴. Examples of shape-selective reactions are shown in photolysis of alkanophenones⁵ and dibenzyl ketone⁶, ring-opening

reaction of 2, 3-epoxy alcohols⁷, alkylation of toluene⁸, and isomerization of m-xylene⁹.

We have been interested in the application of zeolites to organic reactions in the liquid phase. In the addition of water and alcohols to alkenes, alkylchlorosilane-treated Z-HM (mordenite type)-R showed its capacity of accelerating the reaction to give hydroxy- and alkoxy-substituted products with suppression of the formation of by-products¹⁰. H-Z-HM15 showed its capacity of performing the ring-opening reaction of epoxides¹¹⁻¹⁴, especially 1, 2-epoxybutane with methanol besides shape-selective property¹², where the highest regioselectivity for the formation of 2-methoxybutanol was observed. Z-HM (mordenite type) was also effective catalyst for hydrolysis of esters¹⁵⁻¹⁷, where esters were effectively converted to the corresponding acids and alcohols.

Zeolites resulted in effective catalysts for nucleophilic reactions such as hydrolysis, alcoholysis of esters.

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Hydrolysis of water-insoluble aliphatic esters with straight chains¹⁵, esters having some rings^{18, 19}, and lactones¹⁹ was catalyzed by H-ZSM-5 in toluene/water solvent system. Octadecyltrichlorosilane-treated H-ZSM-5, H-ZSM-5-C₁₈, showed its capacity of accelerating the reaction of aliphatic esters. In the case of esters having rings the pronounced acceleration of the reaction came to be observed by use of cyclohexyltrichlorosilane-treated H-ZSM-5, H-ZSM-5-^oC₆. The shape-selective properties of zeolites in catalysis have been evaluated by comparing the reaction rates over the zeolites with that over SiO₂-Al₂O₃ catalyst or in HCl solution. The shape-selectivity became higher with increase in a size of substrate for diffusion into the pore of zeolite. The substrates having the diameter larger than 5.6 Å, significantly larger in size than the pore openings of ZSM-5, could not react in this system. The selectivity was unequivocally attributed to the size of substrate^{15, 18, 19}. Transesterification²⁰ of ethyl acetate by alcoholysis (C_nH_{2n+1}OH: n=1-6) readily proceeded by H-Z-HM15 (mordenite type) catalyst accompanying the shape-selectivity.

This paper reports the application of H-Z-HM15 for a nucleophilic reaction of acylation of amines by aminolysis of esters (Scheme 1), where the catalyst performs the reaction accompanying the shape-selective property.

2. Experimental

2. 1. Materials

ZSM-5s (Mobile Oil Co., distributed as “standard” catalyst samples from the Catalysis Society of Japan), zeolites of Y type (Z-HY5.6) and mordenite type (Z-HM20) (“standard” catalyst samples of the Catalysis Society of Japan), zeolite of faujasite type (F-9) (Wako Chemicals), and SiO₂-Al₂O₃ (JRC-SAL-2; a “standard” catalyst sample of the Catalysis Society of Japan) were dried at 110°C for a day and stored in a desiccator.

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

ZSM-5-70: SiO₂ content 92.7 wt%, Al₂O₃ content 1.7

wt%, Na₂O content 0.82 wt%;

Z-HY5.6: SiO₂ content 72.8 wt%, Al₂O₃ content 22.0 wt%, Na₂O content 3.5 wt%;

Z-HM20: SiO₂ content 91.0 wt%, Al₂O₃ content 7.76 wt%, Na₂O content 0.06 wt%;

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

SiO₂-Al₂O₃ (silica-alumina): 13.8% Al₂O₃, Na₂O content 0.012 wt%).

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

Other materials were commercially available and used as obtained.

2. 2. Catalyst preparation

Each H-zeolite was prepared by a conventional cation exchange procedure using 1.00 mol L⁻¹ NH₄Cl aqueous solution followed by calcination in air at 500°C. For example, H-type zeolite of H-ZSM-5-70 was prepared from ZSM-5-70. Alkyl immobilized H-ZSM-5 (abbreviated as H-ZSM-5-C₁₈, C₁₈ = octadecyl group) was prepared by treating H-ZSM-5 with octadecyltrichlorosilane^{15, 21}.

2. 3. Procedure of acylation and analysis

A typical example of the acylation of amine by aminolysis is illustrative. Na-ZSM-5 (40 mg) and octyl acetate (2.5 mmol) were added to octylamine (10.0 mL) in a 50 mL of flask, and the suspension was refluxed.

Aliquots of the reaction mixture were analyzed on a Yanagimoto Model G900 gas chromatograph with PEG 20M and/or Chromosorb 101 packed column. All the reaction products were identified as being identical with the authentic samples.

2.4. Acid strength

Acid strength of the zeolite catalysts in solvents was



Scheme 1. Aminolysis of esters

measured in the following manner: 10 mg of the catalyst and 5 mL of solvent were put into a flask, 1 drop of 2% ethanol solution of Hammett indicator was added to the solvent, and then the mixture was allowed to stand for 12h at room temperature with occasional shaking. The acid strength was determined visually from the color change of the indicator adsorbed on the catalyst.

3. Results and discussion

3. 1. Activities of zeolites

Various types of zeolites were tested in an aminolysis of octyl acetate with butylamine as a candidate for the catalyst for aminolysis of esters (Table 1). Reaction rate of each catalyst was estimated by the measurement of the formation of the corresponding acetate and octyl alcohol and of the conversion of octyl acetate. All of the catalysts showed appropriate activities for the reaction, and the reaction gave the acetylated product. Zeolite of H-ZSM-5-70, having the highest value of the ratio Si/Al, showed the highest activity in the reaction.

3. 2. Various acetates and some esters with H-ZSM-5-70 catalyst

The H-ZSM-5-70 was applied to the reaction with various acetates in butylamine. The first order-rate constants k in esters to the corresponding amides and alcohols were listed in Table 2. The catalyst exhibited the activity for the reaction with all of the esters. H-ZSM-5-70 is the effective catalyst for this reaction. In detail, the catalyst showed higher activities in aliphatic esters than those in esters having some rings.

3. 3. Shape-selective properties in some amines

Various amines were also tested with octyl acetate. The rate constant k and the relative rate constant k_{rel} based on k in propylamine are summarized in Table 3, together with the data using *n*-butyllithium (*n*-BuLi) catalyst. *n*-BuLi was used for an evaluation of shape-selective property of H-ZSM-5-70 to the reaction. Empirically, the shape-selective photolysis of dibenzyl ketone over more bulky catalyst of SiO₂ has been reported to be poor^{22, 23}. Both catalysts showed the activities in primary and secondary amines. The values of k'_{rel} / k_{rel} in the case of primary amines become higher with an increase in a total carbon number of amine. The value in cyclohexylamine was the highest one in three amines. The values of cyclohexylamine and 1-methy butylamine showed fairly high values which mean shape-selective properties of the catalyst H-ZSM-5-70. This is clearly demonstrated in the figure 1 where the value of k'_{n-BuLi} / k'_{ZSM-5} means the same value of k'_{rel} / k_{rel} . Cyclohexylamine has the largest minimum diameter in primary amines, and 1-methy butylamine is secondary amine. The ratio of relative rate constants, k'_{rel} / k_{rel} , donates the relative magnitude of reaction rate which demonstrates the shape-selective property of zeolite to the reactant acetate. A higher value of the ratio means a larger retardation of the rate. The overall reaction rate would depend on the diffusion of the esters to the surface of the H-ZSM-5-70. 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. Factors for causing retardation, such as boiling point and permittivity, appear to be negligible taking into account the comparison with the rate using the alcohols.

Table 1. Aminolysis of octyl acetate with butylamine over various zeolites^a

No.	Zeolite	Ri^b	Si/Al ^c
1	H-ZSM-5-70	8.02	39.0
2	H-ZSM-5-70-C ₁₈	2.93	39.0
3	H-Z-HY5.6	4.93	2.8
4	H-F-9	4.60	1.3
5	H-Z-HM20	3.59	10.1
6	SiO ₂ -Al ₂ O ₃ ^d	3.97	5.3

^a Octyl acetate (2.500 mmol, 0.4307 g) and zeolite (40.00 mg) were added to butylamine (10.00 mL), and the suspension was refluxed.

^b Initial rate of the formation of the corresponding acetyl amine and octyl alcohol., $Ri / 10^{-4} \text{ mol g}^{-1} \text{ h}^{-1}$.

^c The Si/Al atomic ratios of zeolite were calculated on the basis of the SiO₂ and Al₂O₃ contents.

^d 13.8% alumina-SiO₂-Al₂O₃.

Table 2. Aminolysis of esters with butylamine over H-ZSM-5-70^a

No.	Ester		k^b
1	Methyl acetate		44.0
2	Ethyl acetate		15.2
3	Propyl acetate		14.8
4	Butyl acetate		9.7
5	Amyl acetate		14.6
6	Hexyl acetate		13.5
7	Heptyl acetate		20.9
8	Octyl acetate		31.2
9	Cyclohexyl acetate		5.0
10	Methyl phenylacetate		9.9
11	2-Phenylpropyl isobutyrate		3.2
12	Methyl diphenylacetate		4.1

^a Ester (2.500 mmol) and H-ZSM-5-70 (40.00 mg) were added to butylamine (10.00 mL), and the suspension was refluxed.

^b First order-rate constants in esters to the corresponding amides and alcohols / 10^{-2} g-cat⁻¹h⁻¹.

Table 3. Shape-selective aminolysis of octyl acetate with various amines^a

No.	Amine	H-ZSM-5-70		<i>n</i> -BuLi		k'_{rel}/k_{rel}	Minimum diameter ^d /Å
		k^b	k_{rel}^c	k^{*b}	k_{rel}^{*c}		
1	Propylamine		5.1	1	1045	1	4.56
2	Butylamine		31.2	6.1	9616	9.205	4.56
3	Cyclohexylamine		14.1	2.8	6169	5.903	6.18
4	1-Methyl butylamine		12.3	2.4	6087	5.824	4.56
5	1,1-Dimethyl ethylamine		0.0	0.0	0.0	0.0	5.97
6	1,1-Dimethyl butylamine		0.0	0.0	0.0	0.0	5.97

^a Octyl acetate (2.500 mmol, 0.4307 g) and H-ZSM-5-70 (40.00 mg) or *n*-BuLi (0.09608 mg) were added to a certain amine (10.00 mL), and the suspension was refluxed.

^b First order-rate constants / 10^{-2} g-cat⁻¹h⁻¹.

^c Relative rate constants based on the constant in the case of propylamine.

^d Minimum diameters of the substrate molecules of amines were estimated by space filling model.

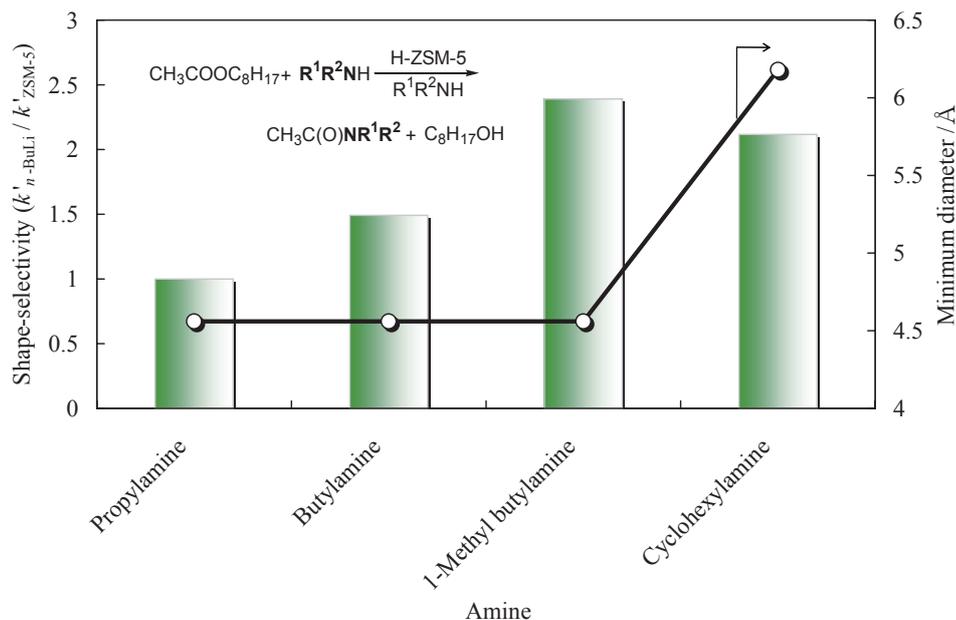


Figure 1. Shape-selective property of H-ZSM-5 to aminolysis of octyl acetate with various amines

The value would be ascribed primarily to the size of the solvent molecule as described before in zeolite-catalyzed ring-opening of functionalized epoxides¹³.

The overall reaction rate would depend on the diffusion of the amines to the surface of the H-ZSM-5-70. The amines with long chains are 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 properties of the zeolite becomes significant. Then the value k'_{rel} / k_{rel} would reflect shape-selective property of H-ZSM-5-70, taking into account non shape-selective properties of n-BuLi. Thus, the shape-selective property of H-ZSM-5-70 increased in higher amines of primary amine with higher carbon number. The case of 1-methyl butylamine is not clearly explained now

why the retardation occurs.

3. 4. Some nucleophilic reactions in solvolysis

H-ZSM-5 resulted in an effective catalyst for some nucleophilic reactions (Scheme 2) such as aminolysis, alcoholysis, and hydrolysis, and results are summarized in Table 4. Lower reactivities in alcoholysis were observed to some acetates. Hydrolysis of water-insoluble aliphatic acetates with straight chains was also catalyzed by the catalyst in toluene/water solvent system. In the case of this hydrolysis, we have previously reported that octadecyltrichlorosilane-treated H-ZSM-5, H-ZSM-5-C₁₈, showed its capacity of accelerating the reaction of aliphatic esters¹⁵. In the case of esters having rings the pronounced



Scheme 2. Nucleophilic reaction such as hydrolysis, alcoholysis, and aminolysis of esters

Table 4. Solvolysis of some esters over zeolite^a

No.	Ester	k^b		
		Aminolysis	Alcoholysis	Hydrolysis
1	Methyl acetate	44.0	1.1	275.9
2	Hexyl acetate	13.5	1.0	23.0
3	Octyl acetate	31.2	1.4	1.8

^a Ester (2.500 mmol) and H-ZSM-5-70 (40.00 mg) were refluxed in a solvent of each butylamine (10.00 mL), ethanol (10.00 mL), or toluene (5.00 mL)/ water (5.00 mL), respectively.

^b First order-rate constants to the corresponding alcohol from an each ester / 10⁻² g-cat⁻¹h⁻¹.

acceleration of the reaction came to be observed by use of cyclohexyltrichlorosilane-treated H-ZSM-5, H-ZSM-5- C_6 ¹⁹.

3.5. Acid strength

The determination of the acid strength of the zeolite catalysts, which showed higher activities for the acylation, were carried out in various solvents by use of Hammett indicators, and the results are summarized in Table 5. H-ZSM-5-70 has the strongest value in water ($+1.5 \geq H_0 > -3.0$), and the zeolite has the weakest value in ethanol ($+6.8 \geq H_0 > +4.8$). Intrinsic acid strength of zeolite was maintained even treatment of silylation by octadecyltrichlorosilane. The acylation needs a catalyst of acid or base to proceed the reaction. Presumably, H-ZSM-5-70 plays a role of acid catalyst as the catalyst showed the highest activity for the reaction. 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 zeolite can be rationalized as reflective of results 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. Details of the mechanism for the selectivity could not be interpreted clearly at present. Further research on the reaction is under way.

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Oil Co. and the Catalysis Society of Japan) and "standard" catalyst samples of Z-HM20 and Z-HY5.6, and silica-alumina (SAL-2) (by the Catalysis Society of Japan).

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Table 5. Acid strength of H-ZSM-5 and SiO₂-Al₂O₃ in various solvents

Catalyst	Si / Al	Solvent	H_0						
			+6.8	+4.8	+3.3	+1.5	-3.0	-5.6	-8.2
H-ZSM-5-70	39.0	Ethanol	+	-	-	-	-	-	-
H-ZSM-5-70	39.0	Water	+	+	+	±	-	-	-
H-ZSM-5-70-C ₁₈	39.0	Ethanol	+	-	-	-	-	-	-
H-ZSM-5-70-C ₁₈	39.0	Water	+	+	+	+	-	-	-
SiO ₂ -Al ₂ O ₃	5.3	Methanol	+	+	-	-	-	-	-
SiO ₂ -Al ₂ O ₃	5.3	Ethanol	+	+	-	-	-	-	-
SiO ₂ -Al ₂ O ₃	5.3	1-Propanol	+	+	-	-	-	-	-
SiO ₂ -Al ₂ O ₃	5.3	1-Butanol	+	+	-	-	-	-	-
SiO ₂ -Al ₂ O ₃	5.3	1-Pentanol	+	+	-	-	-	-	-
SiO ₂ -Al ₂ O ₃	5.3	1-Hexanol	+	+	-	-	-	-	-

Note. +, Acidic color; ±, slightly acidic color; -, basic color.

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