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Transesterification of Esters such as Ethyl Acetate with Alcohols over Mordenite Type of Zeolite H-Z-HM15

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Abstract

Mordenite type of zeolite H-Z-HM15 resulted in an effective catalyst for the transesterification of esters such as ethyl acetate with alcohols. The shape-selective properties of H-Z-HM15 catalyst were observed for the reaction by the measurement of the reaction rates.

Key words : H-Z-HM15, mordenite type zeolite, transesterification, shape-selective property

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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].

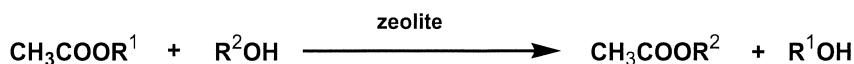
We have been interested in the application of zeolites to organic reactions in the liquid phase. In the addition of water and alcohols to alkenes, alkylchlorosilane-treated Z-HM (mordenite type)-R showed its capacity of accelerating the reaction to give hydroxy- and alkoxy-substituted products with suppression of the formation of by-products [7]. H-Z-HM15 showed its capacity of performing the ring-opening reaction of epoxides [8-11], especially 1,2-

epoxybutane with methanol besides shape-selective property [9], where the highest regioselectivity for the formation of 2-methoxybutanol was observed. Z-HM (mordenite type) was also effective catalyst for hydrolysis of esters [12-14], where esters were effectively converted to the corresponding acids and alcohols. Nishiguchi, *et al.* reported that transesterification of esters with alcohols proceeded in the presence silica-supported metallic sulphates such as $\text{Cs}(\text{SO}_4)_2$ by being heated the reaction mixture [15]. This paper reports the application of H-Z-HM15 to the reaction and presents a quite simple reaction system only by use of the zeolite H-Z-HM15 (Scheme), where the catalyst performs the reaction accompanying the shape-selective property.

2. Experimental

2. 1. Catalyst preparation

Each H-type zeolite of H-Z-HM was prepared from zeolite of each mordenite type Z-HM ("standard" catalyst sample of the Catalysis Society of Japan) by a conventional cation



Scheme. Transesterification of ester with alcohol over zeolite

exchange procedure using 1 mol L⁻¹ NH₄Cl aqueous solution followed by calcination in air at 500°C. All the H-Z-HMs were powder and their chemical properties are listed below.

Z-HM10: SiO₂ content 83.7 wt%, Al₂O₃ content 14.3 wt%, Na₂O content 0.12 wt%;

Z-HM15: SiO₂ content 88.0 wt%, Al₂O₃ content 10.0 wt%, Na₂O content 0.06 wt%;

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

SAL-2 of Silica-alumina (SiO₂-Al₂O₃) ("standard" catalyst sample of the Catalysis Society of Japan: 13.8% Al₂O₃, Na₂O content 0.012 wt%) was used after drying at 110°C for a day.

2. 2. Procedure of transesterification and analysis

A typical example of the transesterification of ester is illustrative. H-Z-HM15 (40 mg) and ethyl acetate (2.5 mmol) were added to a methanol (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 MS capillary column, FFAP capillary column, and/or PEG 20M packed column. Tryphenylmethane was used as an internal standard for analyses. All the reaction products were identified as being identical with the authentic samples.

3. Results and discussion

3. 1. Ethyl acetate and other acetates (Shape-selective property)

Mordenite type of zeolite in various ratio of silica to alumina such as H-Z-HM10, H-Z-HM15, and H-Z-HM20 were tested for the transesterification of ethyl acetate with methanol. The reaction rates were observed by the measurement of the formation of methyl acetate and of the conversion of ethyl acetate. The first order-rate constants in ethyl acetate *k* are listed in Table 1. H-Z-HM15 exhibited the activity for the reaction.

Table 1. Transesterification of ethyl acetate with methanol over H-ZM zeolites^a

No.	Catalyst	<i>k</i> ^b
1	H-Z-HM10	0.00
2	H-Z-HM15	6.30 ^c
3	H-Z-HM20	0.00

^a The suspension of ethyl acetate (2.5 mmol) and catalyst (40 mg) in methanol (10 ml) was refluxed.

^b First order-rate constant in ethyl acetate / 10⁻³ g⁻¹ h⁻¹.

^c Initial rate *R*_i equals 1.58 x 10⁻⁵ molg⁻¹ h⁻¹.

Table 2. Various acetates^a

No.	CH ₃ COOR R	H-Z-HM15		SAL-2 ^b		Shape-selective property (<i>k</i> ' _{rel} / <i>k</i> _{rel})
		<i>k</i> ^c	<i>k</i> ' _{rel} ^d	<i>k</i> ^c	<i>k</i> ' _{rel} ^d	
1	CH ₃	11.23	1	21.77	1	1
2	<i>n</i> -C ₃ H ₇	0.35	0.03	4.97	0.23	7.67
3	<i>n</i> -C ₄ H ₉	0.25	0.02	6.45	0.30	15.00
4	<i>n</i> -C ₆ H ₁₃	0.19	0.02	4.03	0.19	9.50
5	<i>n</i> -C ₇ H ₁₅	0.00	0.00	4.58	0.21	∞
6	<i>n</i> -C ₈ H ₁₇	0.00	0.00	3.00	0.14	∞
7	<i>n</i> -C ₁₂ H ₂₅	0.00	0.00	3.42	0.16	∞

^a The suspension of acetate (2.5 mmol) and H-Z-HM15 or SAL-2 (40 mg) in ethanol (10 ml) was refluxed.

^b SiO₂-Al₂O₃ (13.8% Al₂O₃).

^c First order-rate constant / 10⁻² g⁻¹ h⁻¹.

^d Relative rate constant.

The H-Z-HM15 was applied to the reaction with various acetates in ethanol. The rate constant *k* and the relative rate constant *k*_{rel} based on *k* in methyl acetate are summarized in

Table 2, together with the data using silica-alumina (SiO₂-Al₂O₃). SAL-2 of SiO₂-Al₂O₃ was used for an evaluation of shape-selective property of H-Z-HM15 to the reaction.

Activities of both catalysts become lower with an increase in a total carbon number of the esters. The value k'_{rel} / k_{rel} becomes higher with an increase in the total carbon number of esters. The highest value ∞ was found in the case of esters having more than carbon number 7 (No.5 in Table 2).




The overall reaction rate would depend on the diffusion of the esters to the surface of the H-Z-HM15. 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 properties of the zeolite becomes significant. Then the value k'_{rel} / k_{rel} would reflect shape-selective property of H-Z-HM15, taking into account the

little shape-selective properties of SiO₂-Al₂O₃. Empirically, the shape-selective photolysis of dibenzyl ketone over SiO₂ has been reported to be poor [16, 17]. Thus, the shape-selective property of H-Z-HM15 increased in higher esters with higher carbon number.

3. 2. Lactones

Transesterification of more bulky ester of lactone was tested in the same manner as the section 3.1, and the results are summarized in Table 3. A retardation of the reaction was observed predictably in the most bulky lactone of oxacyclotridecan-2-one (No. 3 in Table 3), *i.e.* rate constant

Table 3. Lactones^a

No.	Substrate		H-Z-HM15		SAL-2 ^e		S^f (k'_{rel} / k_{rel})
	Structure	Diameter ^b / Å	k^c	k_{rel}^d	k'^c	k'_{rel}^d	
1		5.27	11.23	1	21.22	1	1
2		6.23	45.71	4.07	105.10	4.95	1.22
3		8.32	0.00	0.00	0.00	0.00	—

^a The suspension of substrate ester (2.5 mmol) and H-Z-HM15 or SAL-2 (40 mg) in ethanol (10 ml) was refluxed.

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

^c First order-rate constant / 10⁻² g⁻¹ h⁻¹.

^d Relative rate constant.

^e SiO₂-Al₂O₃ (13.8% Al₂O₃).

^f Shape-selective property.

k equals 0, though the shape-selective property could not evaluate. Slight effect of the shape-selective property was observed in the lactone of 1,2-hydrocoumarin (No. 2) with the higher carbon number.

3. 3. Dependence of Alcohols

The reaction of ethyl acetate in various alcohols was measured with H-Z-HM15. The rate constant k and the relative rate constant k' based on k in methanol are listed in Table 4, accompanying the data using SiO₂-Al₂O₃. The

Table 4. Various alcohols^a

No.	ROH		H-Z-HM15		SAL-2 ^b		Shape-selective property (k'_{rel} / k_{rel})
	R	bp/°C	k^c	k_{rel}^d	k'^c	k'_{rel}^d	
1	CH ₃	64.7	0.63	1	3.88	1	1
2	<i>n</i> -C ₃ H ₇	97	1.98	3.14	16.00	4.12	1.31
3	<i>n</i> -C ₄ H ₉	117.7	3.09	4.90	36.37	9.37	1.91
4	<i>n</i> -C ₅ H ₁₁	136-138	14.74	23.40	134.1	34.56	1.48
5	<i>n</i> -C ₆ H ₁₃	156.5	14.30	22.70	241.0	62.11	2.74

^a The suspension of ethyl acetate (2.5 mmol) and H-Z-HM15 or SAL-2 (40 mg) in alcohol (10 ml) was refluxed.

^b SiO₂-Al₂O₃ (13.8% Al₂O₃).

^c First order-rate constant / 10⁻² g⁻¹ h⁻¹.

^d Relative rate constant.

reactivity increased in higher alcohol, where the highest reaction rate was observed in *n*-hexanol (No. 5 in Table 4). Activities of both catalysts become higher with an increase in a total carbon number of the alcohols. The value $k'_{\text{rel}} / k_{\text{rel}}$ also becomes higher with increase in the total carbon number of alcohols. The highest value 2.74 was found also in the case of *n*-hexanol (No. 5). 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. The value would be ascribed primarily to the size of the solvent molecule as described before in zeolite-catalyzed ring-opening of functionalized epoxides [10].

H-Z-HM15 was the effective catalyst for transesterification of aliphatic acetate and alcohols and showed its shape-selective property for the reaction. The ratio of relative rate constants, $k'_{\text{rel}} / k_{\text{rel}}$, 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-Z-HM15. 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. 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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