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Hydration of cyclohexene by alkyl-immobilized H-ZSM-5 catalyst in decalin–water system

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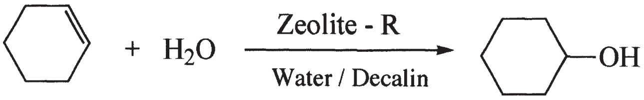
In the hydration of cyclohexene, alkylchlorosilane-treated ZSM-5s, which floated at the interface of the two liquids, were observed to be solid interface catalysts in a decalin–water system. The catalysts, especially cyclohexyl-immobilized H-ZSM-5, show their capacity of accelerating the hydration with suppression of the formation of by-products such as dicyclohexyl ether.

Keywords: alkyl-immobilized H-ZSM-5, hydration of cyclohexene, solid interface catalysts

1. Introduction

Chemical processes using liquid acids such as sulfuric acid, hydrofluoric acid, and aluminum chloride present disposal or toxicity problems. In place of these processes, clean chemical processes usig solid acids are desirable [1]. The application of solid acids further makes separation processes easy. Among solid acids, environmentally friendly oxide-based solid acids are required [2], but they generally lose their activities in water due to poisoning of water. ZSM-5 zeolite is a strong solid acid in aqueous solution and is expected to have a high activity as a catalyst. A notable finding as for water-tolerant catalysis by solid acid is hydrolysis of ester catalyzed by H-ZSM-5 [3]. After that, hydration of butenes by H-mordenite [4], hydration of epoxide to diol by Nb_2O_5 [5], hydrolysis of ethyl acetate by supported heteropoly compounds [6], and hydrolysis of esters [7] and hydration of epoxides [8] by H-ZSM-5 have been reported. Asahi Chemical Ind. has developed a commercial process for hydration of cyclohexene using H-ZSM-5 in water [9]. Ishida et al. inferred that the hydration of cyclohexene proceeded in the pores of H-ZSM-5 and the formation of dicyclohexyl ether was greatly suppressed by the shape-selectivity [10]. Recent work by Okuhara et al. reveals that H-ZSM-5 is a specially active catalyst for the hydration of cyclohexene in excess water [11]. This paper reports that alkylchlorosilane-treated ZSM-5 could further accelerate the hydration of cyclohexene in the liquid phase with suppression of the formation of by-products such as dicyclohexyl ether.



Scheme 1.

2. Experimental

2.1. Catalyst preparation

ZSM-5s (Mobile Oil Co., distributed as “standard” catalyst samples from the Catalysis Society of Japan), zeolites of Y type (Z-HY) and mordenite type (Z-HM) (“standard” catalyst samples of the Catalysis Society of Japan), zeolites of A type (A-4) and faujasite type (F-9) (Wako Chemicals) were used for the reaction. All the zeolites were in powder form and their chemical properties have been cited in a previous paper [7b]. Each H-zeolite was prepared by a conventional cation exchange procedure using 1.00 $\mathrm{mol\,l^{-1}}$ NH_4Cl aqueous solution followed by calcination in air at 500 °C. For example, H-type zeolite of H-ZSM-5-70 was prepared from ZSM-5-70Na. Alkyl-immobilized H-ZSM-5 (abbreviated as H-ZSM-5-R, R = alkyl group) was prepared by treating H-ZSM-5 with alkylchlorosilane [12].

2.2. Procedure of hydrolysis and analysis

The following hydration of cyclohexene is illustrative. H-ZSM-5-R (80 mg) and cyclohexene (15.0 mmol, 123 mg) were added to a mixture of decalin (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 G2800 gas chromatograph with MS capillary column and/or PEG 20M packed column.

3. Results and discussion

Various types of zeolites were used for the hydration of cyclohexene, and the results are summarized in table 1.

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Table 1
Hydration of cyclohexene over various zeolites.[a]

Zeolite	SiO_2/Al_2O_3[b]	R_i[c]
H-A-4 (4A type)	0.5	0.00
H-F-9 (faujasite type)	0.7	0.07
H-Z-HY4.8 (Y type)	5.2	0.00
H-Z-HY5.6 (Y type)	5.6	0.03
H-Z-HM10 (mordenite type)	9.9	0.00
H-Z-HM15 (mordenite type)	14.9	0.04
H-Z-HM20 (mordenite type)	19.9	3.44
H-ZSM-5-70	92.5	9.56
H-ZSM-5-1000	1246.1	1.19

[a] Cyclohexene (15.0 mmol) and zeolite (80.0 mg) were added to a mixture of decalin (5.0 ml) and water (5.0 ml) solvents. Then the suspension was refluxed.

[b] The SiO_2/Al_2O_3 molar ratios of zeolites were calculated on the basis of the SiO_2 and Al_2O_3 contents.

[c] Initial rate $\times 10^{-5}$ (mol g_{cat}^{-1} h^{-1}).

Table 2
Silylation effect on the hydrolysis.[a]

Zeolite	Silylating reagent	R_{rel}[b]
H-ZSM-5-70	non	1[c]
H-ZSM-5-70-C_6[c]	$C_6H_{11}SiCl_3$	9.1
H-ZSM-5-70-ϕ	$\phi SiCl_3$	6.7
H-ZSM-5-70-ϕ_3	ϕ_3SiCl	5.8
H-ZSM-5-70-$(C_1)_2$	$(CH_3)_2SiCl_2$	4.8
H-ZSM-5-70-C_8	$C_8H_{17}SiCl_3$	4.3
H-ZSM-5-70-C_{18}	$CH_3(CH_2)_{17}SiCl_3$	2.8
H-ZSM-5-70-$\phi(E_tO)$	$\phi Si(OC_2H_5)_3$	2.7
H-ZSM-5-70-$\phi_3(E_tO)$	$\phi_3SiOC_2H_5$	2.3
H-ZSM-5-70-$C_8(E_tO)$	$C_8H_{17}Si(OC_2H_5)_3$	0.9
H-ZSM-5-70-$C_{18}(E_tO)$	$CH_3(CH_2)_{17}Si(OC_2H_5)_3$	0.7

[a] Reaction conditions are as in table 1.

[b] Relative rate: $R_{rel} = R_{i\,\text{H-ZSM-5-70-R}}/R_{i\,\text{H-ZSM-5-70}}$.

[c] Initial rate R_i was equal to 9.56×10^{-5} mol g_{cat}^{-1} h^{-1}.

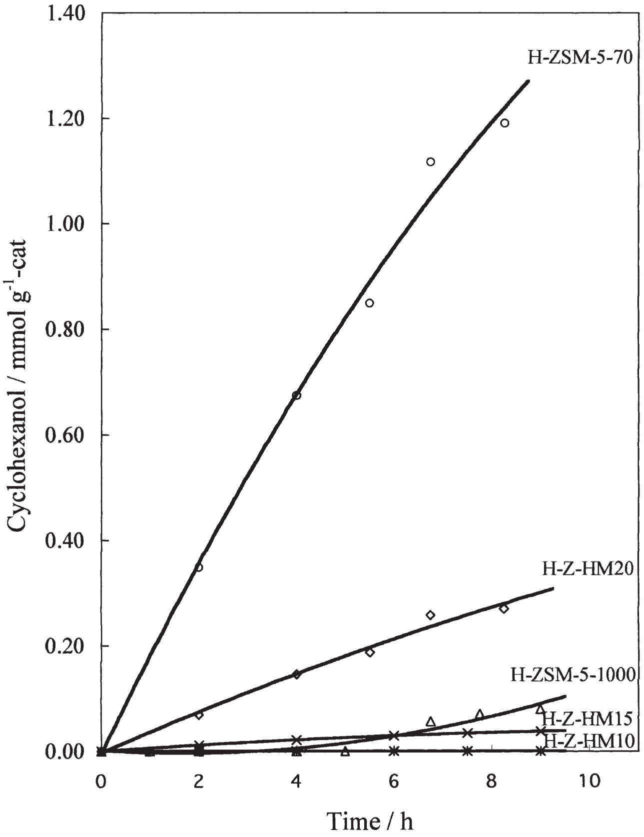

Figure 1. Time courses of cyclohexene hydration over H-ZSM-5 and H-Z-HM zeolites.

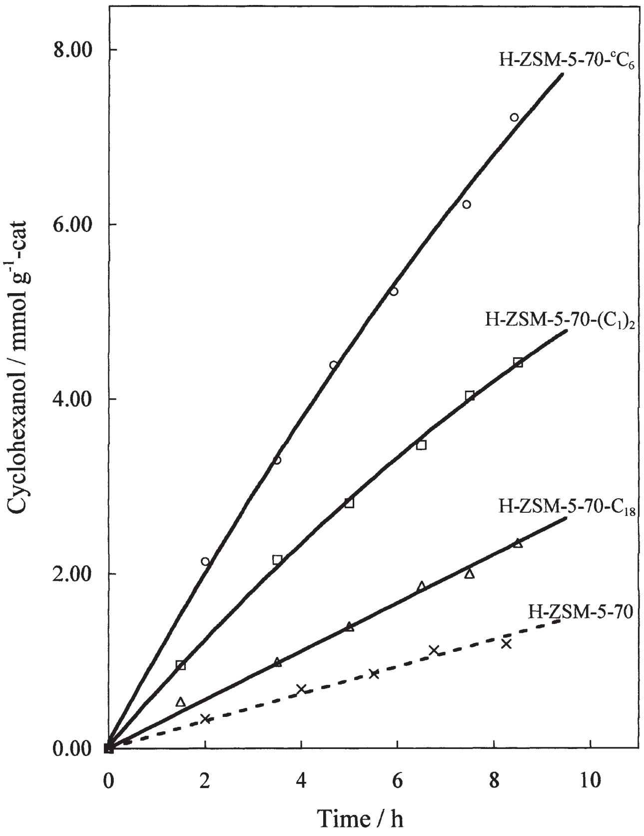

Figure 2. Time courses of cyclohexene hydration over alkyl-immobilized H-ZSM-5.

Time courses of the hydration over H-ZSM-5s and H-Z-HMs are illustrated in figure 1. Zeolites which have higher ratio of SiO_2/Al_2O_3, more than ca. 20, show the activity for the hydration. Especially, H-ZSM-5-70 exhibited the highest activity. In the case of H-Z-HM type of zeolites, the higher SiO_2/Al_2O_3 ratio of the zeolite exhibits higher activity.

H-ZSM-5-70 was an effective catalyst for the hydration and alkyl-modified H-ZSM-5-70 catalysts prepared with various kinds of silylating reagents were tested for the hydration. H-ZSM-5-70-R floated on the decalin–water interface while the non-alkylated H-ZSM-5 was in suspension in the water. Reaction rates were measured, and relative ratios R_{rel} based on the initial rate (R_i) of the formation of cyclohexanol over H-ZSM-5 are listed in table 2 besides the time courses of the hydration in figure 2. Reagents having cyclic alkyl were more effective than those having aliphatic alkyl. The most pronounced effect of the treatment was found in the case of cyclohexyltrichlorosilane where the rate increased by ca. 9.1 times. Reagents having the similar molecular structure to the substrate cyclohexene are effective. The high efficiency of cyclohexyltrichlorosilane treatment was caused presumably by the increase of interactions between the H-ZSM-5-70 catalyst and cyclohexene as mentioned in a former paper [7]. Table 2 also shows that chlorosilane reagents are more effective than the corresponding ethoxide reagents. Cl^- anion, which was produced upon the preparation of the alkylated zeolites, or dealumination of H-ZSM-5 might influence the activities of catalysts. Thus, the alkyl-immobilized H-ZSM-5 performed a catalysis with its capacity of accelerating the hydration of cyclohexene with suppression of the formation of by-products such as dicyclohexyl ether.

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