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High selectivity of MCM-22 for cyclopentanol formation in liquid-phase cyclopentene hydration

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Abstract

Highly effective formation of cyclopentanol through the liquid-phase hydration of cyclopentene has been attempted on various zeolites catalysts. MCM-22 zeolite was the most selective catalyst, which actively converted cyclopentene to cyclopentanol with a selectivity up to 99%. The effects on the hydration of catalyst preparation method, reaction atmosphere and temperature have been investigated for the MCM-22 catalysts. On the basis of the effect of reaction atmosphere, the mechanism of liquid-phase cyclopentene hydration was proposed. The thermodynamic equilibrium between cyclopentene and cyclopentanol was suggested to control greatly the cyclopentene conversion. The cyclopentene conversion was increased to 10% by increasing the water/cyclopentene ratio. Poisoning using organic amines with different molecular sizes revealed that the hydration occurred mainly in the 10-membered ring channels of MWW structure, which had an elliptic aperture smaller than that of MFI structure, exhibiting a significant shape selectivity by suppressing the etherification cyclopentanol.
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Keywords: Liquid-phase hydration; Cyclopentene; MCM-22; Shape selectivity

1. Introduction

The hydration of olefins to alcohols is a typical acid-catalyzed reaction which has been conducted in many ways. The conventional process using sulphuric acid is widely practiced. Nevertheless, it has several serious disadvantages, such as the corrosion of the apparatus, the necessity to dilute the acid with large amount of water to recover the alcohol product, and the consequent requirement to reconcentrate the acid before being recycled. To overcome these disadvantages, it has been proposed to hydrate olefins directly on various solid acid catalysts instead of liquid acids. Phosphoric acid deposited on either silica gel, clay or tungsten oxide, is typical example of such previously attempted solid catalysts. Although these catalysts obviate the handling problems imposed by sulfuric acid, they in turn tend to introduce new complications, notably the comparative production of a large amount of undesirable polymer and ketone. Phosphoric acid in particular is easily eluted during the reaction and then requires that makeup acid should be added to the feed to maintain a constant catalyst activity. Furthermore, such catalysts generally need to be used at temperatures above about 533 K to obtain satisfactory yields and selectivities [1]. There have been some attempts to improve the hydration catalyst using tungsten oxide, molybdenum promoted silica-alumina and cation-exchange resins; however, their activities are not satisfactory enough to replace the heterogenised phosphoric acid, and especially the organic ion-exchange resins lack thermal stability at temperatures above 423 K [2,3].

Y zeolites ion-exchanged with chromium and rare-earth cations and highly siliceous zeolites of ZSM series were reported to successfully catalyze the direct hydration of C_2–C_4 olefins under moderate pressure [4,5]. Zeolites, having unique cation-exchange properties, strong surface acidity, and good thermal stability, are presumed to update the industrial processes of gas-phase hydration.

For the liquid phase hydration of olefins, such as cyclohexene, hydration has been shown to proceed over both homogeneous and heterogeneous acidic catalysts. Sulfuric acid, phosphoric acid, or p-toluenesulfonic acid, in the presence of additives such as copper(II) acetate, zinc(II) acetate, or zinc(II) chloride, produces cyclohexanol with 70% selectivity at ca. 35% conversion of cyclohexene [6]. This process suffers, however, the disadvantage of forming high molec-

ular weight by-products which are difficult to be removed from the reactor. Another problem encountered is that since cyclohexanol and catalyst exist in the aqueous acid phase, the dehydration of cyclohexanol back to cyclohexene occurs to a great extent during the distillation of this phase. The selectivity of cyclohexene hydration depends significantly on the competition between the desirable hydration reaction and other side reactions, such as oligomerization, etc. In order to decrease the extent of undesirable reactions, microporous inorganic, or organic catalysts with shape-selectivity if possible, are preferred to be applied as heterogeneous acid catalysts.

Although the hydration of cyclohexene catalyzed by polymer funtionalized with perfluorosulfonic acid or strong acid polymer resulted in ca. 4% conversion and 80% selectivity at 458 K [7], the real breakthrough in this reaction has not been made until the last decade. Asahi Chem. Ind. has industrialized the production of cyclohexanol from benzene via partial hydrogenation and subsequent hydration which are catalyzed by Ru and zeolite catalysts, respectively. The new process for cyclohexanol production is superior to the conventional two-step oxidation process in the respects of selectivity, safety, corrosion, and energy consumption. The key points of the second step, i.e., the hydration of cyclohexene, are to take the advantages of ZSM-5 zeolite catalyst which is hydrophobic due to the siliceous character and exhibits a distinct shape-selectivity derived from its medium pores. ZSM-5 catalyst performed in the liquid bi-phase system at 393 K gives 13 wt.% yield and 99% selectivity for cyclohexanol [8,9]. This innovative process has fundamentally changed the methods for producing the intermediates of adipic acid and ε-caprolactam in the manufacture of nylon 6.

Liquid-phase cyclohexene hydration is up to now one of only a few slurry processes using zeolite catalysts. Making full use of various zeolite catalysts is expected to develop new process for the production of other alcohols such as cyclopentanol, which is an important intermediate chemical in fragrant industries and a starting material for the production of δ-valerolactam in nylon 5 manufacture.

However, ZSM-5 seems to lack the shape selectivity for formation of cyclopentanol in cyclopentene hydration due to the small molecular size of cyclopentene molecules compared to 10-membered ring (MR) channels of MFI structure. We have revealed recently that MCM-22 zeolite is a promising catalyst for the selective formation of cyclopentanol from cyclopentene hydration [10]. This process may lead to the development of a new environmentally benign industrial process using zeolite catalyst. In this study, we have investigated in details how reaction conditions, synthesis method, and acidity influence the performance of MCM-22 catalysts. The main purpose is to clarify why high shape-selectivity was obtained with the structurally diverse MCM-22.

2. Experimental

2.1. Preparation of zeolite catalysts and characterization

The MCM-22 zeolites were hydrothermally synthesized by modifying the procedures reported previously [11]. Synthesis gels were prepared from hexamethyleneimine (HMI, TCI) or piperidine (PI, Wako) as a structure directing agent (SDA), fumed silica (Cab-o-Sil M7D or Aerosil 200), sodium aluminate (52.1 wt.% NaOH, 27.7 wt.% Al, Wako), sodium hydroxide (Koso), and deionized water. The following example, corresponding to the catalyst No. 1 in Table 1, represents the synthesis procedure. To a mixture containing 26.5 g of silica, 3.84 g of NaOH, and 158 g of H_2O was added 39.3 g of HMI dropwise under vigorous stirring. A solution of 2.82 g of $NaAlO_2$ in 158 g of water was added after 1 h, and the mixture was stirred continuously until producing a homogenous gel with a molar composition of $SiO_2 : 0.033\ Al_2O_3 : 0.3\ NaOH : 0.9\ HMI : 40\ H_2O$. The resulting gel was transferred into an autoclave which was then rotated at 60 rpm and heated at 413 K for 7 days. The solid product was filtered, washed, and dried at 353 K overnight to obtain a lamellar precursor of MCM-22. Then the lamellar product was calcined at 813 K for 8 h to remove SDA to obtain MCM-22. Other MCM-22 samples were synthesized in similar ways from the gels with molar composition shown in Table 1. Y, Beta, mordenite (MOR), ZSM-5 and ferrierite (FER) were obtained commercially.

Table 1
Synthesis and characterization of various MCM-22 zeolites[a]

Sample name	Type of SDA[c]	Gel composition[b]		SiO_2/Al_2O_3		N_2 adsorption	
		SiO_2/Al_2O_3	Na/SiO_2	As-syn.	Ion-exchanged	A_{Lang} (m^2 g^{-1})	V_p (cm^3 g^{-1})
MCM-22-HMI-30	HMI	30	0.3	23	23	685	0.16
MCM-22-HMI-50	HMI	50	0.2	44	43	635	0.15
MCM-22-PI-50	PI	50	0.19	43	44	614	0.14
MCM-22-HMI-60	HMI	60	0.15	54	54	610	0.14
MCM-22-PI-60	PI	60	0.15	55	55	565	0.13
MCM-22-HMI-100	HMI	100	0.18	99	98	526	0.12

[a] Crystalization conditions: temperature, 423 K; time, 7 days; rotating, 60 rpm.
[b] SDA/SiO$_2$ = 0.9, H$_2$O/SiO$_2$ = 40.
[c] HMI: Hexamethyleneimine, PI: Piperidine.

All the zeolites were transformed into proton-form by the conventional ion-exchange method. A calcined sample was treated with 0.2 N NH_4NO_3 solution for 2 h at 353 K five times. Ion-exchanged samples were calcined at 773 K (except for Y, which was calcined at 723 K) for 5 h before being employed as catalysts in the hydration reaction.

MCM-22 samples were characterized by SEM, XRD, ICP elemental analysis, IR spectroscopy, temperature programmed desorption of ammonia (NH_3-TPD), and N_2 adsorption. XRD patterns were collected using a MAC Science MX-Labo X-ray diffractometer (Cu-K$_\alpha$ radiation). Scanning electron micrograph (SEM) images were recorded on a JEOL Electron Probe X-ray microanalyser (JXA-8900RL). The chemical composition of samples was analyzed by a Shimadzu ICPS-8000E ICP atomic emission spectrometer. The IR spectra were collected on an FT-IR Perkin Elmer 1700 series spectrometer. NH_3-TPD was carried out on a Bel Japan REX-P2000 instrument, equipped with a quadrupole mass spectrometer (M-QA100F, ANELVA). N_2 adsorption isotherms were obtained on a Bel Japan BEL SORP 28SA instrument.

2.2. Cycloalkene hydration

The liquid-phase hydration of cycloalkene was carried out batch-wise in a 50 cm^3 teflon-lined autoclave. For a typical run, 0.3 mol of water, 0.06 mol of cycloalkene and 1 or 2 g of catalyst were mixed in the reactor. The reaction was carried out by heating the reactor under vigorous stirring at 373–413 K for 6–120 h. In some cases, the reaction is performed under Ar atmosphere in a glove box. After the reaction the product mixture was extracted with ether, in which cycloheptanone as an internal standard was added. The mixture was then analyzed on a gas chromatograph (Shimadzu 14A) equipped with an OV-1 capillary column (0.25 mm, 50 m long, df 1.5 μm). The products were determined on a gas chromatograph-mass spectrometer (JEOL DATUM-JMS-AX 500).

3. Results and discussion

3.1. Characterization of MCM-22 catalysts

MCM-22 is generally synthesized by using hexamethyleneimine (HMI) as an SDA [11]. ERB-1 with the same topology as MCM-22, on the other hand, is synthesized with piperidine (PI) but requires the presence of crystallization supporting agent of boric acid [12]. We have tried here from the first time the synthesis of MCM-22 using PI as an SDA under boric acid-free conditions.

MCM-22 catalysts exhibited similar aggregated platelet morphology irrespective of SDAs as revealed by SEM images (not shown). The XRD patterns of all the samples were identical to those given in Ref. [13], identifying them as MCM-22. The SiO_2/Al_2O_3 ratios determined by ICP
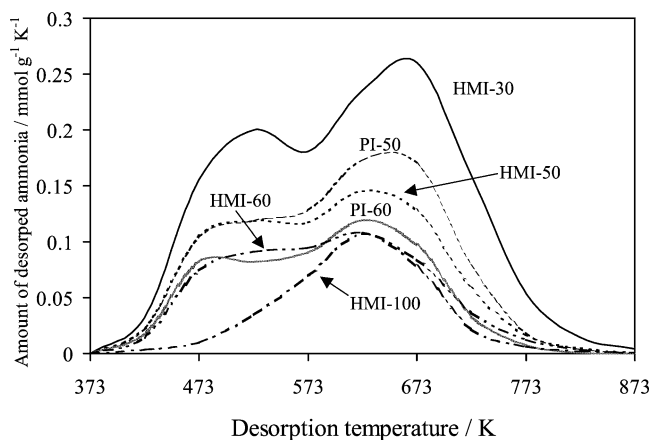

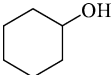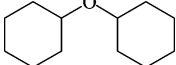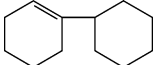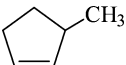Fig. 1. NH_3-TPD profiles of MCM-22 catalysts.

showed no significant difference between the as-synthesized and the ion-exchanged MCM-22 samples (Table 1). The IR spectra of MCM-22 in the hydroxyl vibration region showed a strong band at 3745 cm^{-1} due to the terminal silanol groups, [SiOH], and a band at 3610 cm^{-1} due to the bridging hydroxyl groups, [Si(OH)Al] (not shown). The 3610 cm^{-1} band decreased in intensity gradually with decreasing Al content, indicating a decrease in the amount of Brønsted acid sites.

NH_3-TPD spectra of MCM-22 samples consist of two peaks at 423–573 K and 573–723 K (Fig. 1), corresponding to weak and strong acid sites, respectively. The lower temperature peak decreased remarkably with decreasing Al content. This peak is probably attributed to weak Lewis acid sites generated by partial dehydroxylation of structural Si(OH)Al groups at high temperature. Indeed, this type of Lewis acid sites reversibly return to Brønsted acid sites upon adsorption of water [14]. The higher temperature peak mainly due to the Brønsted acid sites of framework Al decreased gradually with decreasing Al content. The specific surface area and pore volume of MCM-22 samples, measured from N_2 adsorption isotherms at 77 K, where in the range of 526–685 m^2 g^{-1} and 0.12–0.16 cm^3 g^{-1}, respectively (Table 1). Although the surface area decreased slightly with increasing SiO_2/Al_2O_3 ratio due to the difficulty in crystallizing high silica MCM-22, the values over 500 m^2 g^{-1} indicated that all the samples had good quality.

3.2. Hydration of cyclohexene and cyclopentene over various zeolite catalysts

Cyclohexene and cyclopentene were hydrated in the liquid-phase with a proton-type zeolite catalysts to give the corresponding alcohols as shown in Tables 2 and 3. These experiments were carried out in the air. However, the presence of oxygen greatly influenced the product selectivity as described in the later section. The products were predominately cycloalcohol, dicycloalkyl ether and cycloalkene dimers. Table 2 shows that ZSM-5 was the most effective catalyst for the cyclohexene hydration among the

Table 2
Cyclohexene hydration catalyzed by various zeolite catalysts[a]

Catalyst (SiO$_2$/Al$_2$O$_3$ ratio)	Conv./ mol %	Selectivity/mol %			
		⬡—OH	⬡—O—⬡	⬡—⬡	⬠—CH$_3$
Y (14)	2.4	83.8	6.9	4.8	4.6
Beta (25)	9.2	64.5	22.0	13.0	0.6
MOR (17)	3.0	92.5	2.5	3.0	2.0
ZSM-5 (25)	13.4	97.8	0.1	0.1	1.9
FER (20)	0.5	82.4	1.7	2.2	13.7
MCM-22 (30)–HMI[b]	5.9	96.8	0.4	1.1	1.7

[a] Reaction conditions: catalyst, 2 g; cyclohexene : H$_2$O : catalyst (weight ratio) = 4.8 : 5.4 : 2.0; temperature 393 K; time, 18 h; under air atmosphere.
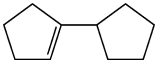[b] HMI: hexamethyleneimine was used as SDA.
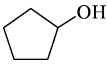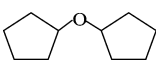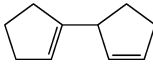
zeolite catalysts investigated since it showed the highest conversion and more importantly, the highest selectivity to cyclohexanol. The advantages of ZSM-5 must originate from the medium pores of 10-MR and the hydrophobic nature because of the high silica form. The latter property allows ZSM-5 to serve as a water-tolerant solid acid catalyst showing high catalytic activity, while the former makes ZSM-5 exhibit a shape selectivity by suppressing the successive reaction of cyclohexanol with cyclohexene to form ether. These findings are fully consistent with what has been reported by Ishida et al. [15]. MOR and FER zeolites, imposing more significant diffusion limitation for the reactant molecules because of practically one dimensional channels or smaller pores, respectively, were less active than the other zeolites. Y and beta zeolites having the 12-MR channels where dicyclohexyl ether formation occurred easily showed much lower alcohol selectivity than the other catalysts. MCM-22 exhibited cyclohexanol selectivity comparable to ZSM-5, although it showed only a half conversion of cyclohexene.

As shown in Table 3, Beta and ZSM-5 zeolite catalysts converted cyclopentene effectively, but showed lower cyclopentanol selectivity than MCM-22 catalyst. MOR and Y zeolites also lack the cyclopentanol selectivity. These results indicate that their pore sizes are too large to suppress the intermolecular dehydration of cyclopentanol or the etherification between cyclopentene and cyclopentanol

in the channels. FER zeolite with smaller pore size showed relatively high selectivity for alcohol, but cyclopentene conversion was low probably because of significantly restricted diffusion. Different from the cyclohexene hydration, only MCM-22 was an effective catalyst from the viewpoint of selective production of alcohol in the cyclopentene hydration. This was seen more obviously in the time courses of cyclopentene hydration (Fig. 2). The conversion of MCM-22 increased up to 6 h, but was nearly the same when the reaction time was prolonged to 18 h. On the other hand, the conversion always increased with the reaction time in the case of ZSM-5 and Beta. However, in contrast to MCM-22 that maintained the alcohol selectivity above 92% independent of the time, ZSM-5 and Beta showed the selectivity decrease from 77 to 40% and from 58 to 30%, respectively, when the hydration was extended from 2 to 18 h. It should be noted that the conversion on MCM-22 was almost unchanged when the catalyst amount was increased and similar conversion was observed when twice the amount of cyclopentene/water was used. Thus, the lower cyclopentene conversion on MCM-22 is attributed to neither low activity nor easy deactivation. A progressive cyclopentene conversion on ZSM-5 and Beta only occurred through the consumption of cyclopentanol to ether, suggesting that the thermodynamic equilibrium between cyclopentene and cyclopentanol may control the cyclopentene conversion on

Table 3
Cyclopentene hydration catalyzed by various zeolite catalysts[a]

Catalyst (SiO$_2$/Al$_2$O$_3$ ratio)	Conv./ mol %	Selectivity/mol %				
		⬠—OH	⬠=O	⬠—O—⬠	⬠—⬠	⬠—⬠
Y (14)	2.6	73.3	0	19.6	2.9	3.6
Beta (25)	13.0	29.5	0	64.4	0.8	5.3
MOR (17)	3.8	57.8	0	30.5	3.5	6.9
ZSM-5 (25)	8.1	41.0	0	51.9	0.4	1.9
FER (20)	0.7	91.4	1.7	0.8	5.8	0.3
MCM-22 (30)–HMI[b]	2.9	92.3	0.2	3.0	3.9	0.6

[a] Reaction conditions: catalyst, 2 g; cyclopentene : H$_2$O : catalyst (weight ratio) = 4.0 : 5.4 : 2.0; temperature, 393 K; time, 18 h; under air atmosphere.
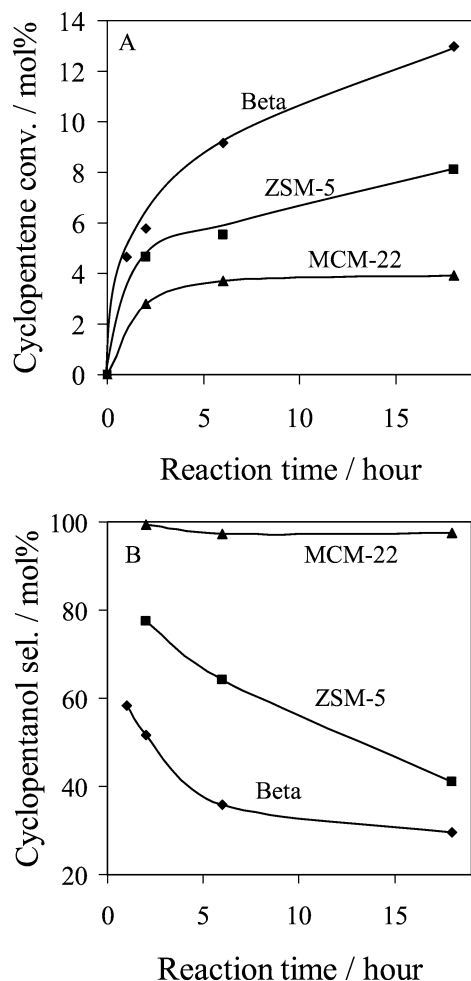[b] HMI: hexamethyleneimine was used as SDA.

Fig. 2. Dependence of cyclopentene conversion (A) and cyclopentanol selectivity (B) on the reaction time. For the reaction conditions, see Table 3.

MCM-22. Detailed consideration of this subject will be given below.

The above results indicated that MCM-22 exhibited an outstanding cyclopentanol selectivity not shared by the other zeolite catalysts. Thus, detailed studies have been carried out to investigate how various parameters affected the catalytic performance of MCM-22 in the cyclopentene hydration.
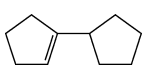
3.2.1. Effect of reaction atmosphere
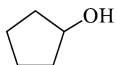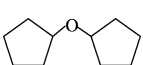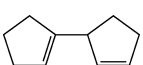
When the cyclopentene hydration was carried out under Ar instead of air, the cyclopentanol selectivity increased to as high as 98% as a result of a dramatic decrease in the se-

lectivity of dimeric by-product, 1,3′-bicyclopentenyl while the cyclopentene conversion on MCM-22 was comparable (Table 4). This result can be interpreted by the reaction mechanism proposed in Scheme 1. The main product of cyclopentanol is produced through the interaction of water with the carbenium intermediate species formed by the protonation of cyclopentene on the zeolitic Brønsted acid sites (Scheme 1a). The carbenium ion would also react with the product cyclopentanol and the reactant cyclopentene to give cyclopentyl ether and the cyclopentene dimer, respectively. Both the side reactions produce the bulky by-products, requiring the open reaction space without steric constraint. The formation of the ether in greater quantities relative to the dimer product is probably because the nucleophilic substitution reaction of alcohol to form ether could occur more easily than the dimerization reaction, which makes the selectivity of dicyclopentyl ether higher than the cyclopentene dimer. The noticeable formation of 1,3′-bicyclopentenyl and 2-cyclopentenone in the presence of oxygen is presumed to occur via the oxidative route (Scheme 1b). Non-catalytic oxidation at the allylic positions of cyclopentene occurs easily at elevated temperature to produce a hydroperoxide intermediate. With the assistance of zeolite acidity, the hydroperoxide with high reactivity changes rapidly into the dimer or unsaturated ketone by-products. Therefore, in order to obtain high alcohol selectivity, it is necessary to carry out the hydration reaction in inert gas atmosphere to suppress the oxidation products. The oxidation pathway shown for cyclopentene substrate (Scheme 1b) is not applicable to cyclohexene probably because the greater ring strain of cyclopentene results in higher levels of autoxidation relative to cyclohexene.

3.2.2. Effect of SiO_2/Al_2O_3 ratio and MCM-22 preparation methods

Table 5 shows the results of cyclopentene hydration over MCM-22 catalysts prepared using HMI or PI as SDA under Ar atmosphere. Only the ether was the significant by-product. All the MCM-22 catalysts gave the cyclopentanol selectivity over 96% independent of the SiO_2/Al_2O_3 ratio and the preparation method. Except for MCM-22-HMI-60 which showed a lower conversion of 2.6%, the catalytic activity declined slightly for both series of MCM-22 catalysts with increasing SiO_2/Al_2O_3 ratio, namely decreasing Al content. This is as expected because MCM-22 with higher SiO_2/Al_2O_3 ratio contained less acid sites as revealed by

Table 4
Effect of reaction atmosphere on cyclopentene hydration[a]

Reaction atmosphere	Conv./ mol %	Selectivity/mol %				
		⟨OH⟩	⟨=O⟩	⟨O⟩	⟨⟩	⟨⟩
Air	3.3	93.2	0.6	1.2	4.6	0.3
Ar	3.5	98.4	0	0.7	0.6	0.2

[a] Reaction conditions: MCM-22 (SAR = 22), 1 g; cyclopentene : H_2O : catalyst (weight ratio) = 4.0 : 5.4 : 1.0; temperature, 393 K; time, 18 h.
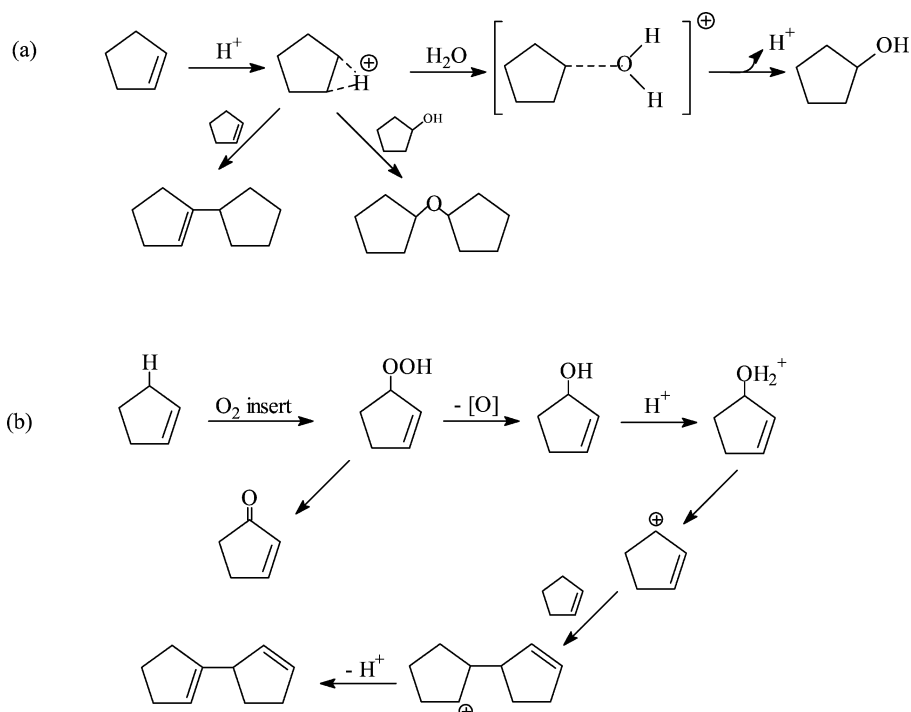
Scheme 1. Reaction routes of cyclopentene hydration (a), and the side reactions in air (b).
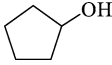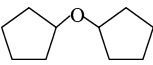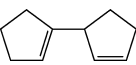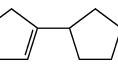
NH$_3$-TPD measurements (Fig. 1). It is surprising that MCM-22-HMI-100 showed a relatively high conversion of 3.1% considering it possesses the smallest amount of acid sites. An increase in hydrophobicity at high SiO$_2$/Al$_2$O$_3$ ratio, the property important for the effective function of solid acid in aqueous solution, may partially account for this behavior. However, the potential ability of MCM-22 seemingly has not been displayed fully even at high Al content due to the thermodynamic limitation on the hydration.

MCM-22-PI catalysts showed somewhat higher conversion than those prepared by HMI at similar SiO$_2$/Al$_2$O$_3$ ratios (Table 5, no. 2, 3, 5, and 6). The amounts of strong Brønsted acid sites determined by NH$_3$-TPD for MCM-22-PI-50 and MCM-22-HMI-50 were 0.55 and 0.44 mmol g^{-1}, respectively. This suggests that PI is more effective than HMI in incorporating Al species into the frameworks to form the Brønsted acid sites.

3.2.3. Effects of hydration temperature

The cyclopentene hydration is an exothermic reaction, which was confirmed by the lower conversion obtained at 413 K than at 393 K (Table 6). High conversion was thus expected if the reaction is carried out at lower temperature which would be favorable for the equilibrium conversion to cylopentanol. However, at 373 K the conversion increased with the time very slowly and reached only 4.1% even after the reaction for 120 h. The hydration occurred more slowly at reaction temperature lower than 373 K (not shown). The acid sites of zeolites hardly act as catalytic centers for the liquid-phase olefin hydration at temperature lower than 373 K probably because of the strong adsorption of water molecules. Another possible reason may be that the energy barrier in the protonation of alkenes is hardly overcome at low temperature.
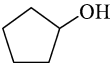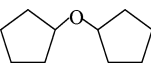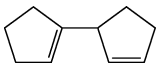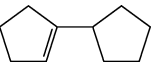
Table 5
Cyclopentene hydration catalyzed by MCM-22 catalyst prepared by HMI and PI[a]

No.	Catalyst[b]	SiO$_2$/Al$_2$O$_3$	Conv./ mol %	Selectivity/mol %			
				OH	O		
1	MCM-22-HMI-30	23	3.7	98.2	0.8	0.7	0.3
2	MCM-22-HMI-50	43	3.2	97.2	1.7	0.8	0.3
3	MCM-22-HMI-60	54	2.6	96.7	2.1	0.8	0.4
4	MCM-22-HMI-100	98	3.1	95.7	3.4	0.7	0.3
5	MCM-22-PI-50	44	3.7	97.4	1.6	0.7	0.3
6	MCM-22-PI-60	55	3.4	97.4	1.7	0.6	0.3

[a] Reaction conditions: catalyst 1 g; cyclopentene : H$_2$O : catalyst (weight ratio) = 4.0 : 5.4 : 1.0; temperature, 393 K; time, 18 h; under Ar atmosphere.
[b] HMI (hexamethyleneimine) or PI (piperidine) was used as SDA.

Table 6
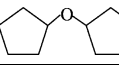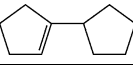Effect of temperature and time on the cyclopentene hydration over MCM-22 catalyst[a]

Temp./ K	Reaction times/h	Conv./ mol %	Selectivity/mol %			
			⬠–OH	⬠–O–⬠	⬠═ ⬠	⬠═ ⬠
393	18	4.2	98.3	1.1	0.4	0.2
413	18	3.4	95.8	2.8	1.0	0.4
373	18	1.5	98.9	0.3	0.6	0.1
373	72	3.3	99.1	0.4	0.4	0.1
373	120	4.1	98.7	0.8	0.4	0.1

[a] Reaction conditions: MCM-22 ($SiO_2/Al_2O_3 = 24$), 1 g; cyclopentene : H_2O : catalyst (weight ratio) $= 4.0 : 5.4 : 1.0$; under Ar atmosphere.

3.2.4. Effect of thermodynamic equilibrium

We have made great efforts to increase the cyclopentanol yield on MCM-22 catalyst by varying the SiO_2/Al_2O_3 ratio, preparation methods and reaction conditions such as time and temperature as described above, but the conversion varied little and the cyclopentanol yield never exceeded 4%. This maximum yield was also the case in the reaction catalyzed by the other zeolites. Thus, these results bring out the problem of thermodynamic equilibrium between cyclopentene and cyclopentanol. Since thermodynamic data depending on temperature and pressure are lacking and the complicated situations for the reaction do not allow us to determine correctly the existing phases for the reactants and products, it is hard to calculate the equilibrium. We have tried to estimate the equilibrium composition by carrying out the dehydration of cyclopentanol, i.e., the reaction reverse to cyclopentene hydration (Table 7). The same conditions as in the hydration were employed for the dehydration of cyclopentanol except for the replacement of cyclopentene with cyclopentanol. The dehydration of cyclopentanol in the presence of H_2O occurred much more rapidly than the etherification over the three zeolites, while large pore Beta reasonably produced bulky ether more than ZSM-5 and MCM-22. Obviously, the dehydration proceeded more rapidly than the hydration. The lower effectiveness of Beta and MCM-22 compared to ZSM-5 in the dehydration is suggested to be due to the higher hydrophilicity of Beta and the smaller 10 MR channels of MCM-22. The high dehydration level observed on ZSM-5 strongly indicates that the equilibrium is greatly shifted to the cyclopentene side at 393 K. Considering that the dehydration may still have not

reached the end due to the possible deactivation of ZSM-5, 95% cyclopentanol conversion (5% cyclopentanol remaining) matched well with the maximum conversion about (4%) attained in the cyclopentene hydration. Hence, the thermodynamic equilibrium seems to control the liquid-phase hydration of cyclopentene, which makes the conversion higher than 4% impossible under the present conditions. Despite the equilibrium, ZSM-5 and beta zeolite catalysts exhibited 8 and 13% cyclopentene conversion, respectively (Table 3). This is mainly because the alcohol product further reacts with starting material of alkene to form ether.

3.2.5. Effect of water/olefin ratio

In order to shift the equilibrium to the cyclopentanol side to increase the conversion in the cyclopentene hydration, the water/olefin molar ratio was increased while keeping the amount of MCM-22 catalyst constant. The cyclopentene conversion increased from 4% at the normal water/cyclopentene ratio of 5 to 10% at the ratio of 30 while the alcohol selectivity higher than 98% was retained (Fig. 3). It is noteworthy that the industrial process for cyclohexene hydration is operated at similar conversion levels. MCM-22 showed much higher selectivity of cyclopentanol formation
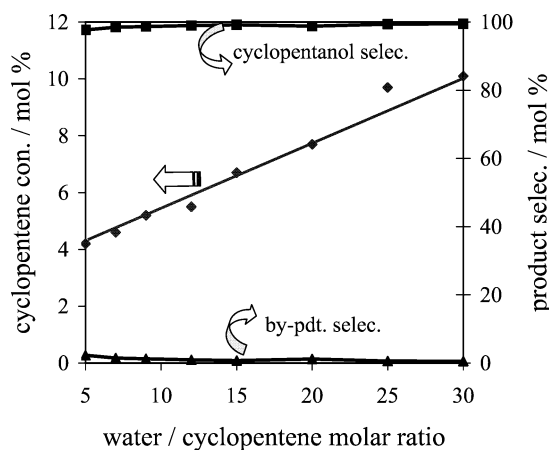
Table 7
Cyclopentanol dehydration catalyzed by zeolite catalysts[a]

Catalyst	SiO_2/ Al_2O_3 ratio	Conv./ mol %	Selectivity/mol %		
			⬠	⬠–O–⬠	⬠–⬠
Beta	25	50	81.0	19.0	0.05
ZSM-5	25	95	93.5	6.4	0.1
MCM-22	24	54	99.9	0.1	0

[a] Reaction conditions: catalyst, 1 g; cyclopentanol : H_2O : catalyst (weight ratio) $= 5.2 : 5.4 : 1.0$ temperature, 393 K; time, 18 h.

Fig. 3. Effect of water/cyclopentene ratio on the cyclopentene hydration over MCM-22 reaction conditions: MCM-22 ($SiO_2/Al_2O_3 = 24$) catalyst 1 g; cyclopentene : catalyst (weight ratio) $= 4.0 : 1.0$; temperature, 393 K; time 18 h; under Ar atmosphere.
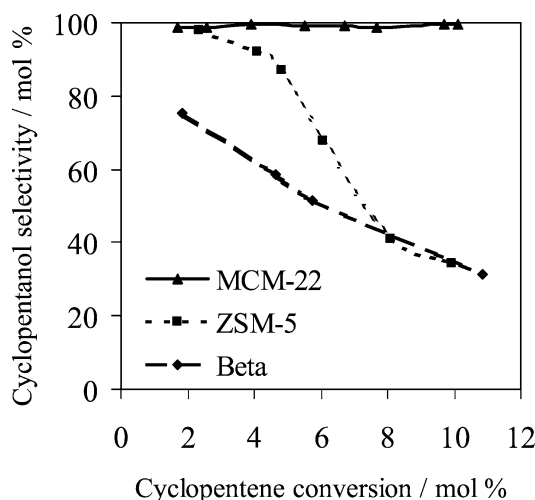
Fig. 4. Cyclopentene hydration over MCM-22, ZSM-5 and Beta; reaction conditions: cyclopentene : H$_2$O : catalyst (weight ratio) = 4.0 : 5.4 − 31.6 : 1.0 − 2.0; temperature, 393 K.

Fig. 5. Channel system of MCM-22.

than ZSM-5 and Beta zeolite catalysts at high cyclopentene conversions (Fig. 4).

3.2.6. An investigation into the high cyclopentanol selectivity of MCM-22

The MWW topology of MCM-22 exhibits structural diversity of side pockets and two independent 10-MR channel systems one of which contains the supercages (Fig. 5). The existence of open reaction spaces which would impose minimal shape selectivity makes it difficult to explain the high alcohol selectivity observed with MCM-22. In order to clarify the MCM-22 active sites contributing to the cyclopentene hydration reaction, poisoning experiments with amines have been carried out. In the presence of trimethylamine (Me$_3$N) which is expected to diffuse into all the acid sites of MCM-22, the cyclopentene conversion decreased to 0.6% (Table 8), indicating the hydration was severely retarded. On the other hand, 2,4-dimethylquinoline (2,4-DMQ) which is believed not to enter into the 10-MR channels but selectively deactivates the acid site within the 12-MR side pockets [16], both the cyclopentene conversion and the alcohol selectivity increased. These results strongly suggest that the cyclopentene hydration occurs mainly within the two 10-MR channels, and the intracrystalline supercages connecting
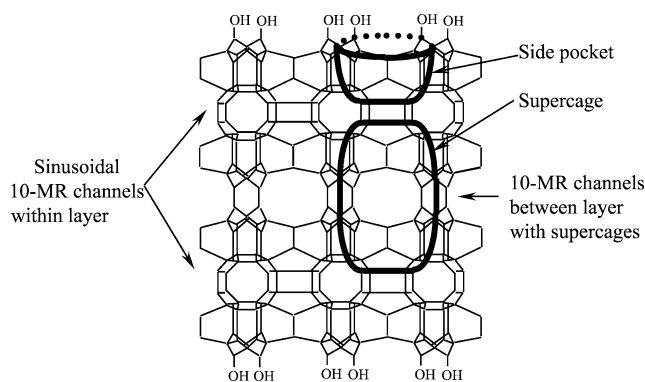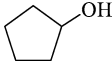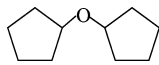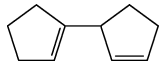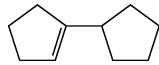
to the outer surface through the interlayer 10-MR channels. The elliptic aperture of these 10-MR channels with a free diameter of 4.0 × 5.5 Å (between layer) and 4.1 × 5.1 Å (within layer), respectively, smaller than the 10-MR channels of MFI structure (5.1 × 5.5 Å and 5.3 × 5.6 Å) [17], would successfully suppress the etherification of cyclopentanol forming bulky ethers. The acid sites at external side pockets would scarcely promote this hydration reaction because the external silanol groups are surrounded by water. MCM-22 is then considered to be characteristic of its 10-MR channels in the liquid-phase hydration. The fact that the poisoning with bulky 2,4-DMQ increased the conversion as well as the selectivity for cyclopentanol would be accounted for by assuming the suppression of the formation of polymeric products which may block the internal active site.

4. Conclusion

MCM-22 proves to be an active and highly selective catalyst for the liquid-phase cyclopentene hydration. The product selectivity depends greatly on the reaction atmosphere; the dimer and unsaturated ketone can be dramatically decreased when the reaction is conducted under Ar atmosphere. MCM-22 synthesized with PI is more effective in catalyzing the hydration than that prepared with HMI. A thermodynamic equilibrium limits the conversion level. However, the alkene conversion and alcohol selectivity can be improved to as high as 10 and 99%, respectively,

Table 8
Poisoning of cyclopentene hydration over MCM-22[a]

Poisoning reagent	Conv./ mol %	Selectivity/mol %			
		OH	O		
No	3.9	97.5	1.5	0.7	0.3
Me$_3$N	0.6	84.4	15.0	0	0.6
2,4-DMQ[b]	4.5	99.6	0.1	0.1	0.1

[a] Reaction conditions: MCM-22 (SiO$_2$/Al$_2$O$_3$ = 24) catalyst, 1 g; cyclopentene : H$_2$O : catalyst (weight ratio) = 4.0 : 5.4 : 1.0; amine, 3 mmol; temperature, 393 K; time, 18 h.
[b] 2,4-DMQ: 2,4-dimethylquinoline.

by increasing the water to olefin molar ratio to 30. The high cyclopentanol selectivity obtained with MCM-22 essentially derives from its 10-MR channels exhibiting high shape selectivity. The side pockets are not considered to significantly contribute to the hydration.

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