Highly Selective Formation of Cyclopentanol through Liquid-Phase Cyclopentene Hydration over MCM-22 Catalysts

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MCM-22 catalyst exhibits an extremely high shape selectivity not observed on other zeolites of MFI, MOR and BEA structures, in that it effectively catalyzes the liquid-phase hydration of cyclopentene at a conversion up to 10% and a cyclopentanol selectivity as high as 99%.

The production of alcohols by the hydration of olefins in the presence of aqueous sulfuric acid is an important and widely used industrial process. Nevertheless, it suffers from several disadvantages, such as the corrosion of the apparatus, and the production of undesirable salts. The difficult handling problems associated with liquid acids can be partially obviated by solidifying the liquid acid such as phosphoric acid impregnated silica, or using organic ion-exchange resins. However, these materials give rise to new problems such as easy release of phosphorus and low thermal stability of resins at elevated temperatures.

Searching for new-type solid acid catalysts for olefin hydration is thus a research subject of great interests. Aluminosilicate zeolites, with high surface acidity, uniform channels of molecular level size and excellent thermal stability, seem to be promising hydration catalysts.[1] Asahi Chem. Ind. recently developed an epoch-making process for cyclohexanol production, *i.e.* the liquid-phase hydration of cyclohexene using ZSM-5 zeolite catalyst, which leads to energy-saving and environmentally friendly new processes for producing the raw materials of ε-caprolactam for Nylon-6 and adipic acid for Nylon-66.[2] This process was developed by fully taking the advantages of the hydrophobicity of high silica ZSM-5 zeolite[3] and the shape selectivity of MFI structure.

The slurry process like cyclohexene hydration is still fewer compared to other gas-solid processes using zeolite catalysts. Making full use of various zeolite catalysts is expected to develop new processes for the production of other alcohols such as cyclopentanol because cyclopentanone, the oxidation product of cyclopentanol, is an important intermediate chemical for perfumes and pharmaceuticals. Here, we report that MCM-22 zeolite is a suitable catalyst for the selective formation of cyclopentanol from cyclopentene hydration, which may expand the possibility of zeolite
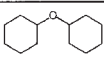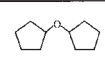
catalysts in this field to result in a new environmentally benign process.

ZSM-5, MOR and Beta zeolites were obtained commercially. MCM-22 was hydrothermally synthesized using hexamethylene-imine as a structure-directing agent according to the previous procedures.[4] All the zeolites were transformed to proton-type by ion-exchange technique using NH_4NO_3 solution. The liquid-phase cycloalkene hydration was carried out batch-wise in a $50\,cm^3$ teflon-lined autoclave reactor. For a typical run, 0.3 mol of water and 0.06 mol of cycloalkene were mixed with 1 or 2 g of catalyst in the reactor. Then the reaction was carried out by heating the mixture under vigorous stirring at 373–413 K for 6–120 h. In some cases, the reaction is performed under Ar atmosphere. The reaction mixture was analyzed by a gas chromatograph (Shimadzu 14A) equipped with a 50 m OV-1 capillary column. The products were determined on a gas chromatograph-mass spectrometer (JEOL DATUM-JMS-AX 500).

Table 1 compares the liquid-phase hydration of cyclohexene and cyclopentene catalyzed by various proton-type zeolites. The experiments were carried out at 393 K under air. The products were predominately cycloalcohol, dicycloalkyl ether and cycloalkene dimer. In the case of cyclohexene hydration, ZSM-5 was obviously a catalyst superior to other zeolite catalysts based on both the conversion and the alcohol selectivity. MOR zeolite showed lower conversion and alcohol selectivity than ZSM-5; it lacks shape selectivity due to the large pores of 12-membered ring (MR). Beta zeolite containing hydrophilic silanols at defect sites and three dimensional 12-MR channels, were also less effective than ZSM-5. These results are consistent with those reported previously, verifying that high-silica ZSM-5 with high hydrophobicity serves as a water-tolerant solid acid catalyst and deeply suppresses the formation of bulky ether and dimer owing to the restricted transition state selectivity derived from the 10-MR channels.[5] Nevertheless, MCM-22 showed comparable cyclohexanol selectivity to ZSM-5, although it was somewhat less active.

In the case of cyclopentene hydration, not only MOR and BEA but also ZSM-5 greatly showed decreased alcohol selectivity probably because their pores are too large to induce the high shape

Table 1. Liquid-phase cycloalkene hydration catalyzed by various zeolite catalysts[a]

Entry	Catalyst (Si/Al$_2$ ratio)	Cyclohexene hydration / mol%				Cyclopentene hydration / mol%			
		Conv.	—OH	—O—	(ene)	—CH$_3$	Conv.	—OH	—O—	(ene)	(dimer)
1	ZSM-5 (25)	13.4	97.8	0.1	0.1	1.9	8.1	41.0	51.9	0.4	1.9
2	MOR (17)	3.0	92.5	2.5	3.0	2.0	3.8	57.8	30.5	3.5	6.9
3	BEA (25)	9.2	64.5	22.0	13.0	0.6	13.0	29.5	64.4	0.8	5.3
4	MCM-22 (25)	5.9	96.8	0.4	1.1	1.7	2.9	92.5	3.0	3.9	0.6

[a]Reaction conditions: catalyst 2 g; cycloalkene : H$_2$O : catalyst (weight ratio) = 4.8 (cyclohexene), 4.0 (cyclopentene) : 5.4 : 2.0; temp., 393 K; time, 18 h.
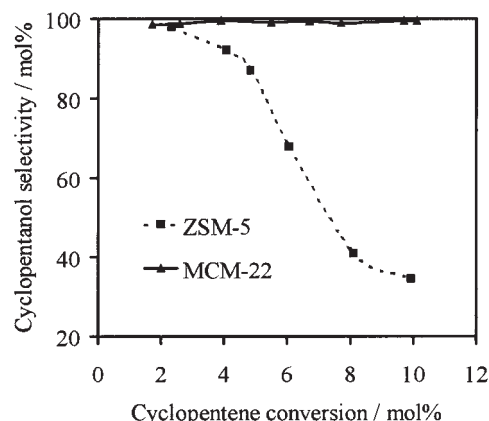
selectivity for cyclopentanol with relatively smaller molecular size. However, MCM-22 maintained the alcohol selectivity higher than 90%, indicating that it is a promising catalyst for producing cyclopentanol selectively.

When the reaction was conducted under Ar atmosphere, the outstanding cyclopentanol selectivity given by MCM-22 was further enhanced to high as 98% as a result of restricting dramatically the formation of 1,2′-bicyclopentene (Table 2, entries 1 and 2). Conceivably, 1,2′-bicyclopentene was formed from the reaction of cyclopentene with the intermediate yielded from the cyclopentene peroxide formed by the allylic oxidation. The reaction at 393 K for 6 h gave nearly 90% of the conversion for 18 h, indicating that initially the reaction rate was fast, and then slowed down probably because of the deactivation or approaching the thermodynamic equilibrium of the reaction between cyclopentene and cyclopentanol. To clarify this issue, the reverse reaction, dehydration of cyclopentanol, was performed over ZSM-5 under the same conditions as Entry 2 in Table 2. Cyclopentanol was readily converted at 95% conversion into cyclopentene and dicyclopentyl ether with selectivity of 94% and 6%, respectively. The equilibrium is thus considered to take the lead in the hydration.

Cyclopentene hydration is an exothermic reaction, which was confirmed by the decrease in the conversion with rising the reaction temperature to 413 K (Table 2, entry 4). High conversion was thus expected by conducting the reaction at low temperature which would be favorable for the equilibrium shift to cyclopentanol. However, the conversion increased with the time very slowly at 373 K (Table 2, entries 5–7), and reached only 4.1% even after the reaction for 120 h. The hydration occurred more slowly at reaction temperatures lower than 373 K (not shown). The acid sites of zeolites seem to hardly act as catalytic centers for the liquid-phase olefin hydration at too low temperatures. Above results suggest that an optimum temperature, *i.e.* 393 K is necessary for the hydration of cyclopentene by taking the balance between the reaction rate and the equilibrium problem.

We found that the hydration was effectively promoted by increasing the water/cyclopentene ratio (Table 2, entries 8 and 9). A conversion was as high as 10%, the same level as the industrialized cyclohexene hydration, was obtained while the alcohol selectivity was higher than 99%.

Figure 1 shows the dependence of cyclopentanol selectivity on the cyclopentene conversion over MCM-22 and ZSM-5. MCM-22 completely suppressed the successive etherification of cyclopentanol, although the MWW structure has open reaction spaces of 12-MR side pockets and supercages besides the independent 10-MR

Figure 1. Cyclopentene hydration over MCM-22 and ZSM-5. Catalyst 1-2 g; water: cyclopentene (molar ratio) = 5–30; temperature, 393 K.
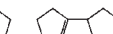
channels. Neither the alkene conversion nor the alcohol selectivity were affected by the selective poisoning of acid sites in open spaces with bulky basic agent of 2,4-dimethylquiniline. This indicates the hydration occurred essentially within the 10-MR channels the aperture of which has a free diameter of 4.0×5.9 Å.[6] The elliptic channels, smaller than the 10-MR channels of MFI structure $(5.4 \times 5.6$ Å), are presumed to be suitable for the shape selective formation of cyclopentanol.

In conclusion, MCM-22 has been found to be an active and highly selective catalyst for cyclopentene hydration. The alkene conversion and alcohol selectivity can be improved to as high as 10% and 99%, respectively, by carrying out the reaction under Ar atmosphere and increasing the mole ratio of water to alkene.

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Table 2. Effect of reaction conditions on the cyclopentene hydration over MCM-22 catalyst[a]

Entry	Reaction atmosphere	Temp. / K	Time / h	H₂O / alkene mol ratio	Conv. / mol%	Selectivity / mol%				
1	Air	393	18	5	3.3	93.2	1.2	0.6	4.6	0.3
2	Ar	393	18	5	4.2	98.3	1.1	0	0.4	0.2
3	Ar	393	6	5	3.7	97.2	2.4	0	0.3	0.1
4	Ar	413	18	5	3.4	95.8	2.8	0	1.0	0.4
5	Ar	373	18	5	1.5	98.9	0.3	0	0.6	0.1
6	Ar	373	72	5	3.3	99.1	0.4	0	0.4	0.1
7	Ar	373	120	5	4.1	98.7	0.8	0	0.4	0.1
8	Ar	393	18	9	5.2	98.7	0.7	0	0.4	0.1
9	Ar	393	18	30	10.1	99.5	0.3	0	0.2	0.1

[a]Reaction conditions: MCM-22 catalyst (Si/Al₂ = 25), 1 g; cyclopentene : catalyst (weight ratio) = 4.0 : 1.0.