Structure modification of mordenite through isomorphous Ti substitution: characterization and catalytic properties

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The introduction of Ti atoms by means of $TiCl_4$ treatment and hydrothermal synthesis has been applied to mordenite zeolite with different structures from silicalite. The incorporation of Ti into the mordenite framework is demonstrated by XRD, FTIR, ^{29}Si MAS NMR techniques, and tested with catalytic oxidation reactions. Ti-Al-mordenite catalyses the oxidation of *n*-hexane, cyclohexane and benzene with hydrogen peroxide under very mild conditions. These reactions can be performed in methanol, acetonitrile and water as solvents. The rate of the reaction is strongly affected by the kind of solvent.

Keywords: Titanium containing mordenite; dealumination; $TiCl_4$ modification; framework incorporation; benzene hydroxylation; phenol; *n*-hexane; cyclohexane oxidation; hydrogen peroxide

1. Introduction

Isomorphous substitution of B, Ga, Fe and Ti into the framework of zeolite causes a change in acidity and a modification in structure altering the products selectivity as a result [1]. Recently titanium substituted zeolites (Ti-silicalites) have been studied with respect to their synthesis, characterization and their catalytic properties [2–5]. The hydrothermal synthesis of titanium silicalite (TS-1) which

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contains titanium atoms in lattice positions has first been claimed by Taramasso and Notari [2].

This material has promising catalytic properties for the epoxidation of alkenes [6,7], the hydroxylation of aromatics [5,8] and the oxidation of alkanes [9] and alcohols [10] with hydrogen peroxide at very mild conditions. Even though successful and consistent crystallization of a pure TS-1 analog of ZSM-5 has been relatively well established, the attempts to incorporate Ti into the mordenite structure and determine its physico-chemical properties are very limited. Kraushaar and Van Hooff [11] reported that titanium silicalite could be obtained from ZSM-5 by dealumination and subsequent treatment with $TiCl_4$. This titanium silicalite exhibited the same catalytic properties as hydrothermally synthesized TS-1 of high purity in the hydroxylation of phenol [8]. Ferrini and Kouwenhoven [12] have reported on the secondary synthesis of Ti modified ZSM-5, zeolite β and Y by reaction with $TiCl_4$ or Ti-tetraisopropylate with H-zeolite samples. It is reasonable to expect that the introduction of titanium atoms by means of $TiCl_4$ treatment may also be applied to highly siliceous large pore zeolites with different structures from silicalite.

In this study, we prepared Ti-Al-mordenite by $TiCl_4$ modification or hydrothermally, and chose the benzene hydroxylation and the *n*-hexane oxidation with hydrogen peroxide as test reactions to examine the catalytic properties. These reactions are known as appropriate test reactions for titanium containing zeolites.

2. Experimental

Fine amorphous silica powder (Zeosil 77 from KoFran Co. 91.8% SiO_2–8.2% H_2O), aluminium isopropoxide (Fluka), titanium tetrabutoxide (Aldrich) and sodium hydroxide (Junsei) were used for Ti-Al-mordenite synthesis. Ti-Al-mordenite samples were synthesized hydrothermally from the substrate compositions of $4Na_2O$–Al_2O_3–(20–30)SiO_2–$0.4TiO_2$–$520H_2O$. Hydrogen peroxide was added to the reaction mixture to obtain titanium in the form of pertitanate species, which were known to be stable in strong basic solutions [3]. The hydrothermal synthesis reaction was carried out in a 250 ml stainless steel autoclave at 448 K, without agitation, for 3 days. Obtained samples were washed, filtered and dried at 393 K for 12 h. The organic material was removed by calcination in air at 823 K. The synthesized Na-type zeolite was ion exchanged with a 1 N NH_4Cl solution and calcined subsequently at 823 K to obtain H-type zeolite.

Titanium modified mordenite was also prepared by treating dealuminated H-mordenite with $TiCl_4$ vapor according to a method reported by Kraushaar and Van Hooff [11]. The Si/Al mole ratios of starting dealuminated H-mordenite were 10, 15 and 64. The reaction with $TiCl_4$ was performed in a vertical quartz reactor. The dealuminated H-mordenite was preheated in a stream of nitrogen (99.9%) overnight at 723 K, and then $TiCl_4$-saturated N_2 was introduced into the reactor at a temperature between 673 and 773 K for 2 h. The sample was purged with nitrogen at 773 K for 6 h after completion of the $TiCl_4$ treatment.

TiO_2/SiO_2 and TiO_2/H-mordenite were prepared by impregnation of supports with $TiCl_4$ solution for the comparison of their catalytic properties. The impregnated samples were dried at 373 K for 3 h and calcined at 973 K for 5 h. Conventional spectroscopic techniques were used for the characterization of Ti modified mordenites. The incorporation of titanium into mordenite was demonstrated by the change in the X-ray diffraction (Philips, PW-1700) and FT-IR spectra (BIO RAD, FTS-40) pattern. UV–VIS diffuse reflectance spectroscopy was performed on a double beam spectrometer using $BaSO_4$ as a standard. ^{29}Si NMR spectra were obtained on a Bruker MSL-200 high resolution spectrometer operating at a field of 4.7 T with a standard magic angle spinning (MAS) probe. The chemical shift was determined from TMS as an external reference. The elemental analysis was done by ICP analysis after dissolution in HF. The hydroxylation of benzene and the oxidation of *n*-hexane with 35% hydrogen peroxide were carried out in a batch reactor at 318 and 323 K, respectively. Products were analysed by gas chromatography (Shimadzu 14-A, FID, Porapak Q, CBP 1 capillary column).

3. Results and discussion

The hydrothermally synthesized Ti-Al-mordenite has essentially the same XRD pattern and framework structure as typical Al-mordenite. No impurity of crystalline structure was detected in the XRD pattern for Ti-Al-mordenite. The result of X-ray diffraction analysis showed that the unit cell parameters decreased after dealumination of H-mordenite and then increased again after subsequent reaction with $TiCl_4$ vapor. The result of X-ray diffraction analysis is shown in table 1. This result is in agreement with the reported characteristics of titanium-silicalite obtained by the reaction of dealuminated ZSM-5 with $TiCl_4$ vapor [11]. Furthermore, Perego et al. [3], Reddy et al. [13] and Thangaraj et al. [14] have observed a linear increase in the unit cell parameter with increasing titanium content for the syntheses of TS-1 and TS-2. This behavior is consistent with the presence of titanium in the framework of zeolite, which is brought about by the

Table 1
Unit cell parameters of H-mordenite, dealuminated mordenite and dealuminated mordenite after reaction with $TiCl_4$ at 773 K

Sample	Si/Al	Si/Ti	Unit cell parameter (nm)		
			a	*b*	*c*
H-mordenite	6	–	1.814	2.049	0.753
dealuminated H-mordenite	64	–	1.808	2.018	0.746
Ti-modified mordenite	64	39	1.810	2.023	0.748

difference between Ti–O and Si–O bond length. The replacement of Si by the larger Ti atoms can cause a slight expansion in the unit cell parameters.

Table 2 summarizes the chemical composition, the amount of adsorbed benzene and BET surface area of mordenites. The high adsorption capacity of $TiCl_4$ modified mordenite is possibly indicative of the absence of partial blocking in the pores by occluded extra-framework titania. The presence of titanium in the framework positions is usually identified by mid IR spectra and ^{29}Si MAS NMR spectra. Fig. 1 shows the IR spectra of titania, normal mordenite (Si/Al = 6), dealuminated H-mordenite (Si/Al = 64), Ti-Al-mordenite treated with $TiCl_4$ and the hydrothermally synthesized Ti-Al-mordenite (Si/Al = 6.4, Si/Ti = 68). IR spectra of mordenites are known [1] to show typical absorption bands at 450 cm^{-1} (T–O bond), 560 and 580 cm^{-1} (double ring), 720 and 800 cm^{-1} (sym. stretching) and 1045, 1223 cm^{-1} (asym. stretching). All the bands shifted to higher frequencies after dealumination of original H-mordenite, and the absorption bands near 800 and 1090 cm^{-1} shifted again slightly toward the lower frequency region after subsequent treatment with $TiCl_4$, as compared with the absorption band of dealuminated H-mordenite. It is expected that the substitution of Ti for Si in the zeolite framework results in an absorption band shift to a lower frequency region owing to the longer Ti–O bond distance as compared with Si–O bond. In addition, as shown in fig. 1, the IR spectra of Ti containing mordenites also exhibited an absorption band near 970 cm^{-1}, which was not found in titania, original H-mordenite and dealuminated H-mordenite. Moreover, the intensity of this peak increased with Ti content in zeolites. Kraushaar and Van Hoof [11] also observed the appearance of a new band at 970 cm^{-1} in the IR spectra of samples treated with $TiCl_4$. The interpretation of spectroscopic data of titanium containing zeolite is discussed elsewhere in the literature [3–5,12–16,18,19]. A characteristic absorption band at about 970 cm^{-1} has been observed in all the framework IR spectra of titanium-silicalites [12–16,18–20]. It was also reported that the intensity of the 970 cm^{-1} band increased as a function of titanium in the lattice and this band was absent in the IR spectra of pure silicalite or titania powder [2,11–14]. This absorption band is attrib-

Table 2
Composition and adsorption capacity of mordenites

Sample	Si/Al	Si/Ti	BET surface area (m^2/g)	Adsorbed benzene amount (wt%) [a]	Exchangeable H^+/unit cell
H-mordenite	6	–	368	8.1	6.9
dealuminated H-mordenite	64	–	415	9.4	0.5
$TiCl_4$ modified Ti-mordenite	64	39	383	8.8	0.4
hydrothermally synthesized Ti-Al-mordenite	6.4	68	352	7.9	6.1

[a] 298 K, 100 mmHg benzene.

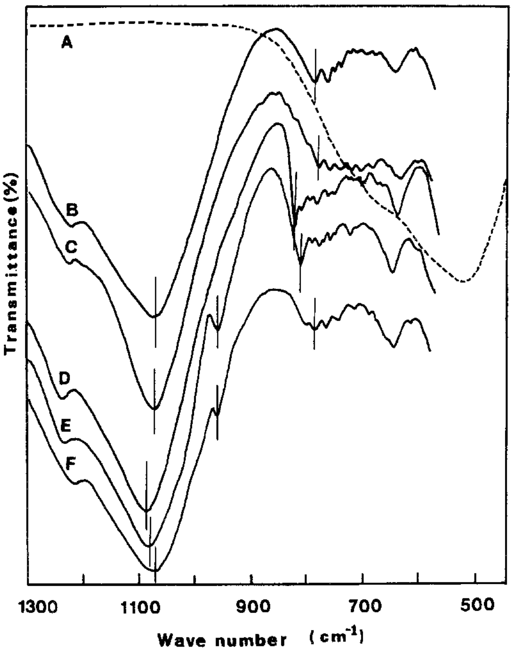

Fig. 1. IR spectra of (A) TiO_2, (B) H-mordenite (Si/Al = 6), (C) TiO_2/H-mordenite, (D) dealuminated H-mordenite (Si/Al = 64), (E) dealuminated H-mordenite after subsequent reaction with $TiCl_4$ at 773 K, (F) hydrothermally synthesized Ti-Al-mordenite (Si/Al = 6.4, Si/Ti = 68).

uted to the =Ti=O group [3,4,15] or an asymmetric stretching mode of tetrahedral Si–O–Ti linkages [16,20] in the zeolite framework. Thus these IR results in fig. 1 may provide evidence for the substitution of titanium into the defective mordenite structure after $TiCl_4$ treatment.

^{29}Si MAS NMR spectra were taken to investigate further evidence for the incorporation of titanium atoms into the mordenite structure. Fig. 2 shows the solid-state ^{29}MAS NMR spectra of dealuminated mordenite (Si/Al = 64) and Ti-Al-mordenites obtained by $TiCl_4$ modification. It has been reported that the peak around −116 ppm is ascribed to Si in distorted tetrahedra containing Si–O–Ti bond [11,14,16], and Thangaraj et al. [14] also reported recently that the intensity and the line broadening of this NMR peak increased with increasing titanium content in the TS-1 system. As shown in fig. 2, the intense ^{29}Si-NMR peak around −113 ppm is attributed to Si bonded to 0 Al, Si(0Al), and the signal at −106 ppm is assigned to Si(3Si, 1Al) or Si(3Si, 0H) structural units in the dealuminated samples. The ^{29}Si MAS NMR signal near −106 ppm due to silanol groups decreased and the spectra exhibited an additional peak at about −116 ppm as a result of $TiCl_4$ treatment. Furthermore, the NMR spectra give a further indication that $TiCl_4$ treatment at higher temperature favours the insertion of titanium atoms. This result is in good agreement with that of ^{29}Si NMR spectra obtained for Ti-silicalite by Kraushaar and Van Hooff [11]. Acid leaching of mordenite can provide highly

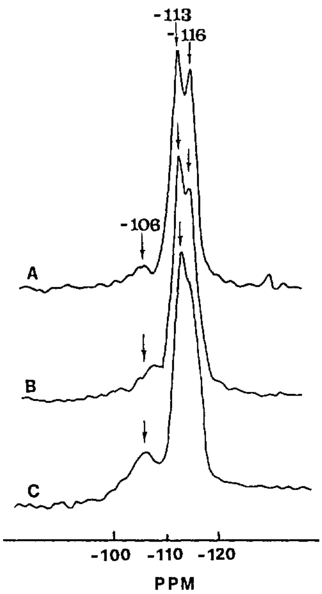

Fig. 2. ^{29}Si MAS NMR spectra of (A) dealuminated H-mordenite after treatment with $TiCl_4$ at 773 K, (B) dealuminated H-mordenite after treatment with $TiCl_4$ at 673 K, (C) dealuminated H-mordenite (Si/Al = 64).

siliceous products with vacant T-atom positions in the lattice which are available for the insertion of titanium atoms, as concluded by the above-mentioned authors [11]. However, in agreement with literature data, the increase in the peak intensity at −116 ppm also strongly supports the incorporation of Ti into the zeolite as a tetracoordinated species.

Fig. 3 shows the UV–VIS diffuse reflectance spectra of titania (anatase), TiO_2/H-mordenite, H-mordenite, $TiCl_4$ modified mordenite and hydrothermally synthesized mordenite. These samples are characterized by absorption bands at wave numbers above 26000 cm^{-1}, which are due to charge transfer transitions between the oxide ions and the empty d-orbitals of Ti^{4+} [19]. In fig. 3, TiO_2 impregnated on H-mordenite shows a strong band at $\sim$ 35000 cm^{-1} which is also present in the TiO_2 spectrum and it can be assigned to titanium in small TiO_2 particles, possibly located inside the pores [19]. $TiCl_4$ modified mordenite and hydrothermally synthesized mordenite have a strong charge transfer band near 50000 cm^{-1}. This absorption band shifted towards higher wave numbers as compared to TiO_2 and TiO_2/H-mordenite. The electron transition at 26000–35000 cm^{-1} is known to be absent in TS-1, and the electronic transition of TS-1 observed at 48000 cm^{-1} is assigned to tetrahedrally coordinated Ti^{4+} by OH and Si–O groups [14,15]. The absorption bands observed at wave numbers higher than $\sim$ 35000 cm^{-1} on the spectra of Ti modified mordenite further confirms the absence of occluded TiO_2 in the pores.

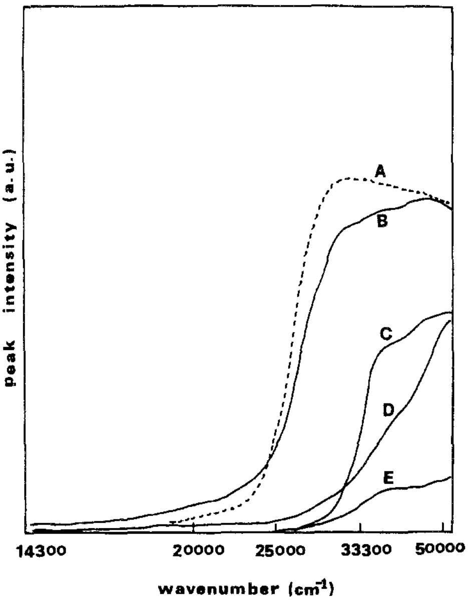

Fig. 3. Diffuse reflectance UV–VIS spectra of (A) TiO_2, (B) TiO_2/H-mordenite, (C) hydrothermally synthesized Ti-Al-mordenite, (D) $TiCl_4$ modified mordenite and (E) H-mordenite.

The hydroxylation of benzene or phenol has frequently been used as a test reaction to characterize the presence of titanium atoms in the framework positions.

It is well known that the catalytic activities and the selectivities in the oxidation of phenol depend on the presence of small amounts of non-framework titania [8,15].

In the presence of non-framework TiO_2, hydrogen peroxide was consumed rapidly by decomposition into H_2O_2 and O_2. The yield of diphenols dropped to almost zero and tar species were formed [15].

The catalytic activities of Na-type and H-type zeolite were examined in the hydroxylation of benzene and in the oxidation of *n*-hexane with hydrogen peroxide and the differences in the catalytic behaviour of the catalysts are compared in table 3. As shown in this table, Na-type zeolite, silicalite, pure titania powder and TiO_2 supported on SiO_2 or H-mordenite showed no catalytic activity at all suggesting that titanium atoms associated with the zeolite framework structure are responsible for the observed catalytic activity. On the other hand, acidic zeolites exhibit an activity only for the reaction of benzene with hydrogen peroxide. Only titanium modified mordenite was active in both reactions. The application of acidic zeolite in the hydroxylation of aromatics has been little explored. H-ZSM-5 is claimed to be an active and selective catalyst by Chang and Hellring [21]. Olah et al. [22] have suggested that acid-catalyzed oxyfunctionalization of aromatics with hydrogen peroxide involves electrophilic hydroxylation with protonated hydrogen peroxide ($^+OH_2$–OH).

Table 3
Benzene hydroxylation and *n*-hexane oxidation with hydrogen peroxide over various catalysts

Catalyst	Conversion [a] (%)	
	benzene [b]	*n*-hexane [c]
H-ZSM-5 (Si/Al = 21)	4.5	nr
H-mordenite (Si/Al = 6)	1.1	nr
HY (Si/Al = 3)	0.7	nr
Na-ZSM-5 (Si/Al = 21)	nr	nr
Na-mordenite (Si/Al = 6)	nr	nr
silicalite (Si/Al > 10000)	nr	nr
TiO_2 (JRC-TiO-5)	nr	nr
TiO_2/H-mordenite	nr	nr
Ti-mordenite	6.2 [d]	5.6 [e]

[a] nr = no reaction.

[b] Benzene/H_2O_2 mole ratio = 1/3, temperature = 313 K, no solvent, 0.07 mole H_2O_2/g-zeolite.

[c] *n*-hexane/H_2O_2 mole ratio = 1, temperature = 323 K, no solvent, 0.07 mole *n*-hexane/g-zeolite.

[d] Benzene/H_2O_2 mole ratio = 5, temperature = 313 K, methanol solvent, 0.07 mole benzene/g-zeolite, solvent concentr.: 70 v/v%.

[e] *n*-hexane/H_2O_2 mole ratio = 1, temperature = 323 K, methanol solvent, 0.07 mole *n*-hexane/g-zeolite, solvent concentr.: 70 v/v%.

In this study, phenol was the only product over acidic H-mordenite and H-ZSM-5. This high selectivity may be ascribed to the protonation of phenol over acid catalysts which suppresses the further electrophilic reaction to obtain dihydroxy benzenes [23]. But the undesirable decomposition of hydrogen peroxide to H_2O and O_2 proceeded at 318 K over H-type zeolites. The acid sites on the zeolite were responsible for H_2O_2 decomposition and the decomposition rates of H_2O_2 decreased in the order of H-ZSM-5 > H-mordenite > H-Y. In contrast, the decomposition of H_2O_2 was not catalyzed by titanium zeolites.

Fig. 4 shows the catalytic properties of Ti-Al-mordenites in the hydroxylation of benzene with hydrogen peroxide. The reaction kinetics were solvent dependent. Benzene hydroxylation could be also performed without any organic solvent over Ti-mordenite. The higher benzene conversion was obtained with methanol solvent, while the conversion value was low with acetonitrile solvent. The selectivity to phenol reached up to 74% over Ti-mordenite both in methanol and acetonitrile solvent and this value is comparable to that obtained over TS-1. Phenol was the only product over acidic H-mordenite as mentioned above, but the secondary product was formed over titanium containing zeolite catalyst.

In addition, the oxidation of *n*-hexane with hydrogen peroxide was performed in methanol and acetonitrile solvent at 323 K respectively, and the conversions of *n*-hexane with reaction time are shown in fig. 5. H-mordenite itself showed no activity in *n*-hexane oxidation at all. As can be seen from figs. 4 and 5, the lower conversion of benzene and *n*-hexane was observed over hydrothermally synthesized Ti-

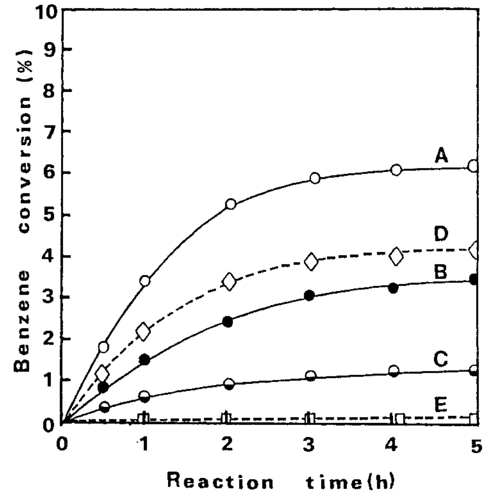

Fig. 4. The hydroxylation of benzene with hydrogen peroxide over $TiCl_4$ modified mordenites (A, B, C), hydrothermally synthesized Ti-Al-mordenite (D) and H-mordenite (E). Reaction temp. 318 K, benzene/H_2O_2 mole ratio = 5, 0.07 mole of benzene/g-zeolite, solvent concentr.: 70 v/v%, solvent: methanol (A, D, E), acetonitrile (B), water (C).

Al-mordenite. This low catalytic activity may probably be explained by the differences in titanium contents and by the undesirable decomposition of H_2O_2 over Brønsted acid sites of Ti-Al-mordenite.

The product of terminal oxidation of *n*-hexane was not detected in the reaction

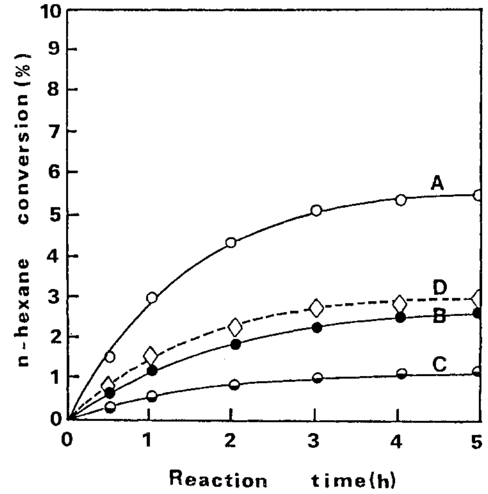

Fig. 5. The oxidation of *n*-hexane with hydrogen peroxide over $TiCl_4$ modified mordenites (A, B, C) and over hydrothermally synthesized Ti-Al-mordenite (D). Reaction temp. 323 K, *n*-hexane/H_2O_2 mole ratio = 1, 0.07 mole of *n*-hexane/g-zeolite, solvent concentr.: 70 v/v%, solvent: methanol (A, D), acetonitrile (B), water (C).

mixture and the selectivities to 2-hexanol, 3-hexanol, 2-hexanone and 3-hexanone obtained over Ti-Al-mordenite in methanol solvent were 31.2, 43.2, 16.4 and 9.2%, respectively. The investigation of the time course revealed that the ratio of ketones to alcohols in the products increased with time as shown in fig. 6. The catalytic activities of Ti-Al-mordenite strongly depended on the kind of solvents. The rates of *n*-hexane oxidation decreased in the order of methanol > acetonitrile > water as solvents. For comparison, the oxidation of cyclohexane was performed over Ti modified mordenite. The conversion of cyclohexane in the reaction with H_2O_2 was 2.8%, and the selectivities to cyclohexanol and cyclohexanone were 41 and 59%, respectively. Cyclohexanone was formed secondary from cyclohexanol, and the oxidation rate of *n*-hexane (fig. 5) was much higher than that of cyclohexane. Tatsumi et al. [17] have found that the oxidation turnover of *n*-hexane over TS-1 catalyst was 17 times as high as that of cyclohexane, and the rate of uptake of cyclohexane by ZSM-5 was significantly smaller than that of *n*-hexane. They [17] concluded that such substrate selectivity presumably arose from the molecular sieve action of TS-1.

In this study, the higher oxidation turnover of cyclohexane (relative to that of *n*-hexane) was obtained over Ti-Al-mordenite as compared with TS-1. This behavior suggests that the pore size of Ti-Al-mordenite allows the rapid diffusion of *n*-hexane, while diffusion of cyclohexane is hindered. Moreover, the narrow pore size of TS-1 contributed toward more severe steric hindrance to diffusion of cyclohexane. This Ti-Al-mordenite can be useful in the oxidation of cyclic hydrocarbons which are restricted to diffuse into TS-1 pores.

Fig. 7 shows that the conversions of *n*-hexane and benzene in the reaction with

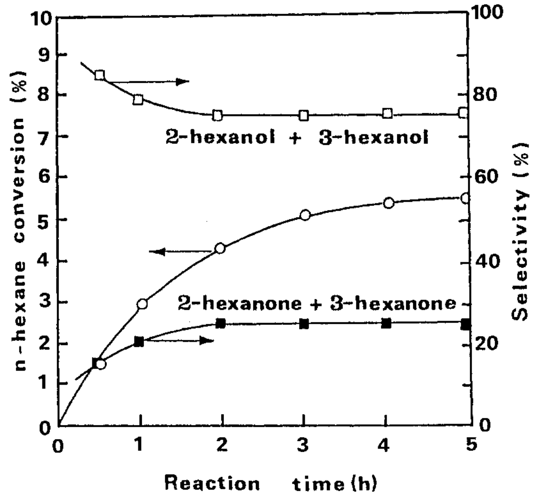

Fig. 6. The product distribution in the oxidation of *n*-hexane with hydrogen peroxide over $TiCl_4$ modified mordenite. Same reaction conditions as for fig. 5 (methanol solvent).

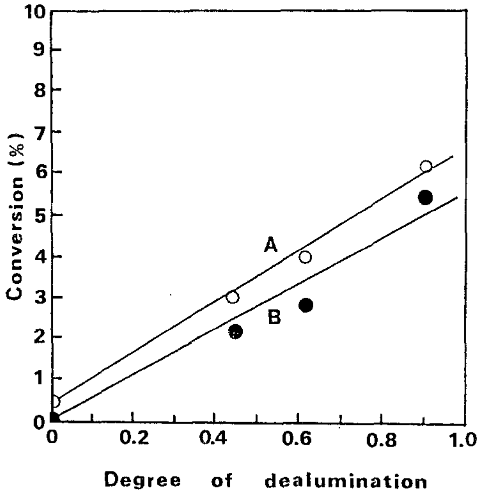

Fig. 7. Effect of degree of dealumination in the reaction of benzene hydroxylation (A) or *n*-hexane oxidation (B). Same reaction conditions as for figs. 4 and 5 (methanol solvent).

H_2O_2 increase with increasing degree of dealumination of mordenites. This improvement in the catalytic activity is believed to result from an increasing content of Ti atoms incorporated into the zeolite framework.

This study has demonstrated the feasibility of Ti substitution into the mordenite framework. Ti-mordenite obtained by modification has similar catalytic properties as compared to those of TS-1.

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