Influence of Fluorine on the Catalytic Performance of Ti−Beta Zeolite

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Treatment of Ti−Beta synthesized by the fluoride method with basic quaternary ammonium solution followed by calcination enhanced the epoxidation activity with hydrogen peroxide, which is due to the reduction of the amount of fluorine contained in the catalyst.

Introduction

Ti−Beta with the BEA structure, having a three-dimensionally accessible large pore system with 12-membered ring (12MR) channels, is found to be more active in the oxidation of bulky substrates such as branched and cyclic alkanes and alkenes using aqueous H_2O_2 or *tert*-butyl hydroperoxide (TBHP) as an oxidant than medium pore TS-1 (MFI structure) because of less diffusion restriction imposed by the large pores. However, a small amount of Al (Si/Al < 200), as a crystallization-promoting element, is generally necessary in the conventional hydrothermal synthesis method for Ti−Beta using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent (SDA).[1,2] The introduction of Al into the Beta frameworks leads to the formation of acid sites. Furthermore, the very complex nature of severely intergrown Beta structure results in a high concentration of silanol groups.[3] These characteristics lead to the high hydrophilicity of Ti−Beta walls, which decreases the oxidation activity for hydrophobic substrates because the pore walls attract water and oxidized product to prevent the contact of the hydrophobic substrates with the active oxidation sites.[4] To reduce the framework Al or defect sites, numerous attempts have been reported: dry-gel conversion,[5−7] cogel,[8] seeding[9] and fluoride methods.[10,11] The fluoride method gives rise to a very hydrophobic Ti−Beta free of framework Al and silanol defects. Although this material has been expected to have high catalytic activity, in the epoxidation of alkenes, the turnover number of Ti−Beta synthesized by the fluoride method was reported to be comparable to hydrothermally synthesized Ti−Beta.[11] One reason might be the larger crystal size obtained by the fluoride method decreasing the effectiveness of the solid catalyst. Koller et al. has reported the existence of five-coordinated Si species, $(SiO)_4SiF^-$, in high-silica zeolites (MFI, BEA, MTW, etc.) synthesized in the fluoride media, as confirmed by the ^{19}F MAS NMR and ^{29}Si{^{19}F} CP MAS NMR techniques.[12] We report here the effect of fluorine on the catalytic activity and a novel postsynthetic method for improving the epoxidation activity of Ti−Beta synthesized by the fluoride method.

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Experimental Section

Ti−Beta(F) was synthesized in the fluoride media according to Camblor et al.[10,11] Calcination was performed at 793 K for 10 h in the stream of O_2 (30 cm^3 min^{-1} g of $solid^{-1}$) to obtain a product with the Si/Ti ratio of 82. Delmotte et al. have reported that fluorine in aluminosilicates and aluminophosphates synthesized in the fluoride medium can be completely removed by the calcination in humid air.[13] Recently, Ishihara et al. have reported that F^- connected to Ti atoms in titania can be removed by anion-exchange treatment with aqueous sodium hydroxide/acetate solution at pH = 12;[14] we adopted their method to remove fluorine in titanosilicate Ti−Beta(F). However, we employed a quaternary ammonium hydroxide instead of sodium hydroxide since alkali cations severely reduce the epoxidation activity of titanosilicates.[15−18] In contrast, quaternary ammonium cations do not poison the active oxidation sites of titanosilicates.[19] Typically, calcined Ti−Beta(F) was treated with 1 mol dm^{-3} aqueous NMe_4OH solution at 353 K for 4 h. The initial pH of the solution was adjusted to ca. 12 by adding acetic acid. Alternatively, the SDA extraction of as-synthesized Ti−Beta(F) was conducted using a pyridine/HCl mixture[20] with the intention of preventing HF from attacking the zeolitic structure in the calcination procedure. Fluorination of hydrothermally synthesized Ti−Beta(OH) was conducted by treating a calcined sample (Si/Ti = 35, Si/Al = 38) with 0.2 mol dm^{-3} aqueous hydrogen fluoride. Calcination at 793 K for 10 h followed all the above liquid-phase postsynthetic treatments. The amount of Ti of both Ti−Beta(F) and Ti−Beta(OH) samples hardly changed throughout these treatments. The liquid-phase epoxidation of cyclohexene and 1-hexene with H_2O_2 was performed batchwise in a round-bottom flask. The amount of fluorine was determined by using a selective fluorine electrode after the complete dissolution of the samples by the alkali fusion.

Results and Discussion

The amount of fluorine in these samples and the results of the liquid-phase epoxidation of cyclohexene and 1-hexene are summarized in Table 1. Directly calcined Ti−Beta(F) contained a relatively high amount of fluorine. SDA extraction with pyridine/HCl resulted in a decrease in the remaining fluorine, and more fluorine was removed by the NMe_4OH treatment followed by calcination. When the as-synthesized Ti−Beta(F) was extracted with pyridine/HCl solution followed by the

TABLE 1: Effect of Postsynthetic Treatment in the Liquid-Phase Epoxidation of Alkenes over Ti−Beta[a]

| entry	synthesis media	treatment	amount of F		cyclohexene		1-hexene	
			wt %	F/Ti	TOF[b]	H_2O_2 eff (%)[c]	TOF[b]	H_2O_2 eff (%)[c]
1	F−	calcined	0.50	1.32	30	63	6	54
2		pyridine/HCl	0.16	0.42	46	78	9	62
3		calcined NMe$_4$OH	0.09	0.24	63	83	14	67
4	OH−	calcined			61	91	10	48
5		calcined HF	0.10	0.11	37	71	6	38
6		calcined HF−NMe$_4$OH	0.008	0.01	50	84	11	44

[a] Reaction conditions: temp, 333 K; time, 1 h for cyclohexene and 3 h for 1-hexene; 8.25 mmol of substrate, 2.5 mmol of H_2O_2 (31 wt % in water), 5 cm^3 of methanol as solvent, and 50 mg of catalyst. [b] Turnover frequency per hour. [c] (Mole of H_2O_2 utilized for oxidation)/(mole of H_2O_2 consumed).
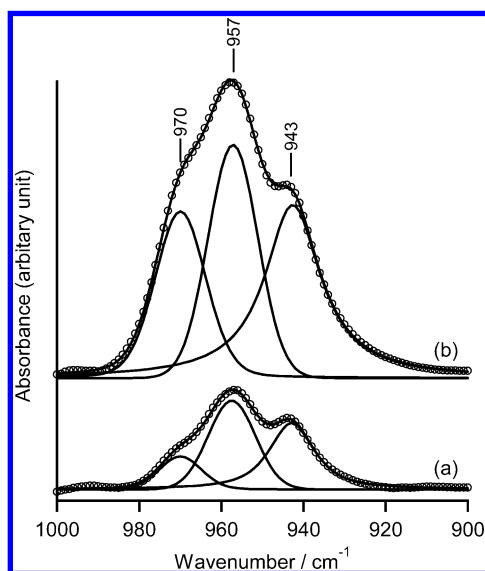
Figure 1. FT-IR spectra of Ti−Beta(F): (a) calcined sample and (b) NMe$_4$OH-treated sample. Open circles and solid lines represent the observed points and the simulated curves, respectively.

calcination, the epoxidation activity was increased (entry 2), and the activity of the Ti−Beta(F) sample was further enhanced by the treatment with NMe$_4$OH solution (entry 3). The NMe$_4$-OH-treated Ti−Beta(F) showed a higher turnover frequency per Ti than the directly calcined Ti−Beta(OH) (entry 4) despite the larger crystal size of Ti−Beta(F) (>2 μm) compared with that of Ti−Beta(OH) (~0.2 μm). This could be due to the beneficial effect induced by the improved hydrophobicity of Ti−Beta(F),[11] which surmounted the detrimental effect caused by its large crystal size. On the other hand, when Ti−Beta(OH) was treated with HF, the epoxidation activity decreased (entry 5), consistent with the observation by Clerici and Ingallina that fluorine adversely affected the activity of TS-1 that was obtained by postsynthetic fluorination of TS-1 with NH$_4$F. [21] By further treating the fluorinated [Ti,Al]−Beta sample with NMe$_4$OAc solution, the epoxidation activity was restored (entry 6). Obviously the epoxidation activity of Ti−Beta(F) and Ti−Beta(OH) was dependent on the amount of fluorine present on the catalyst. The efficiency of hydrogen peroxide was also improved by the treatment with NMe$_4$OH.

FT-IR spectra of Ti−Beta(F) before and after the NMe$_4$OH treatments were collected. The baseline-subtracted spectra in the range 900−1000 cm^{-1} are shown in Figure 1. The spectra were normalized with the area of the peak that could be assigned to the framework vibration (750−850 cm^{-1}). After the NMe$_4$-OH treatment, three bands at 940−970 cm^{-1} increased. The combined peaks were deconvoluted into three pseudo-Voigt functions centered at 943, 957, and 970 cm^{-1}. All of the three peaks increased in intensity after the treatment with NMe$_4$OH
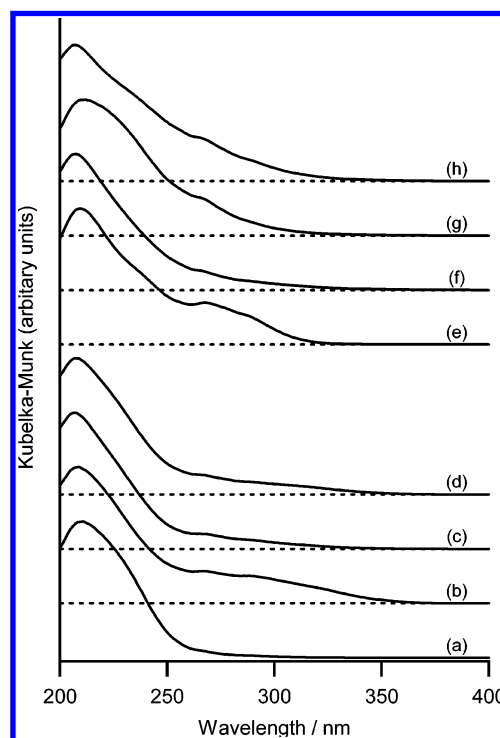
Figure 2. Diffuse-reflectance UV−visible spectra of Ti−Beta synthesized in F− and OH− media postsynthetically treated in various methods: as-synthesized (a), directly calcined (b), py/HCl-treated (c), and NMe$_4$OAc-treated (d) Ti−Beta(F); as-synthesized (e), directly calcined (f), HF-treated (g), and NMe$_4$OAc-treated (h) Ti−Beta(OH).

solution and the increase in the 970 cm^{-1} peak intensity was remarkable. The peak observed at 970 cm^{-1} could be assigned to Si−OH and the other two peaks at 957 and 943 cm^{-1} to Si−O−Ti vibrations.[22] Direct calcination of Ti−Beta(F) and fluorination of calcined Ti−Beta(OH) resulted in the appearance of a broad absorption band in the range 270−290 nm in the UV−visible spectra (Figure 2). This band was reduced in intensity by the defluorination with py/HCl or NMe$_4$OH (Figure 2c,d). The HF treatment of directly calcined Ti−Beta(OH) increased this band (Figure 2g). The UV absorption in this region would be assigned to hexacoordinated Ti species, which could originate from the partial destruction of tetrahedral Ti centers by HF. The treatment with NMe$_4$OH should remove fluorine existing around Ti centers and the following calcination resulted in the condensation to form tetracoordinated Ti species. These FT-IR and UV−visible spectroscopies revealed the increase in the Si−OH and Si−O−Ti groups and the decrease in the Ti species with high coordination number after the treatment with NMe$_4$OH followed by calcination.

The active site for epoxidation is believed to be the titanium hydroperoxo species, and electron-deficient oxygen atom would attack π electron clouds of the olefins. The fluorination of the

SCHEME 1: Postulated Mechanism for the Interconversion of Ti Active Site for the Epoxidation
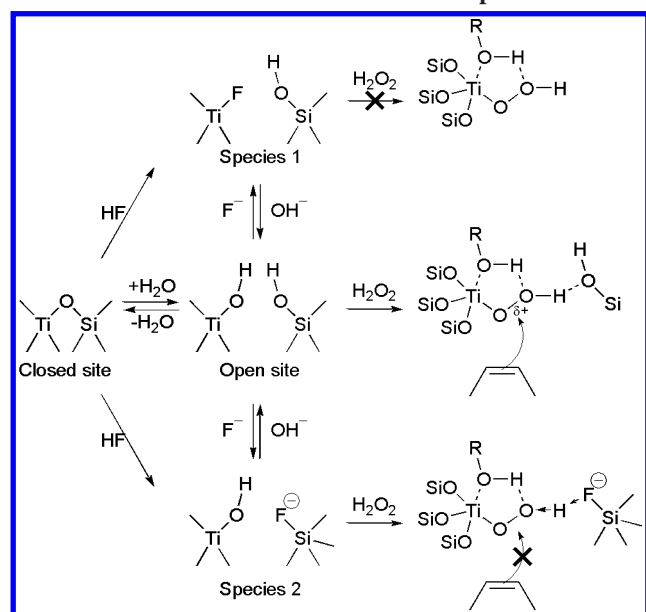
Ti—O—Si would form either species 1 or species 2 in Scheme 1. Species 1 cannot be converted to active intermediates. Species 2 could be converted to titanium hydroperoxo species; however, the negatively polarized fluorine would lower the electrophilicity of the epoxidation active sites by way of hydrogen bonds to decrease the epoxidation ability. It would be reasonable to speculate that the fluoride anion donates electrons to the active site for oxidation of Ti, taking account of KF alumina that has been long known as a strong solid-base catalyst.[23] The removal of fluorine via the ligand conversion of Si—F to Si—OH and/or Ti—F to Ti—OH could increase the amount of the active sites for the oxidation.

Thus we have proved that the presence of the fluorine would be harmful to the catalytic activity of Ti—Beta(F). The catalytic activity of Ti—Beta(F) was effectively improved by defluorination through the treatment with NMe$_4$OH. The present method could be applicable to other titanosilicates synthesized by the fluoride method in order to improve their catalytic activity.

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