Characterization and catalytic properties of Ti-ZSM-5 prepared by chemical vapor deposition

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Ti-ZSM-5 is prepared via a chemical vapor deposition method by reacting HZSM-5 with $TiCl_4$ at temperatures of 200–400 °C. Ti-ZSM-5 is characterized by skeletal- and surface hydroxy-FT-IR, XPS, and XANES spectroscopy. It seems that Ti is incorporated in the zeolite surface with tetrahedral coordination. Contents of incorporated Ti atoms in Ti-ZSM-5 zeolite increase with increasing SiO_2/Al_2O_3 ratio and a CVD reaction temperature of 400 °C is optimal. Cyclohexanone ammoximation was used as test reaction and Ti-ZSM-5 catalysts show similar catalytic activities compared to TS-1.

Keywords: CVD, $TiCl_4$, post-synthesis modification, Ti-ZSM-5, FT-IR, XPS, cyclohexanone, ammoximation

1. Introduction

Titanosilicate having the MFI structure (TS-1) has received considerable attention during the last decade, and has been shown to be an effective catalyst for the selective oxidation of a number of organic substrates using hydrogen peroxide as an oxidant under mild conditions [1–5]. Oxidation reactions over TS-1 are of interest for two reasons: (1) TS-1 is active in several partial oxidation reactions including hydroxylation, epoxidation, ammoxidation, and aromatic oxidation, and (2) aqueous hydrogen peroxide can be used as a green oxidant. Hydrogen peroxide, although relatively expensive, is attractive due to the fact that its by-product is water.

TS-1 is currently used by Enichem for the production of hydroquinone and catechol from phenol [6] and for the synthesis of cyclohexanone oxime from cyclohexanone [7]. The success of TS-1 has induced subsequent research on the synthesis of Ti-containing micro- and mesoporous materials either by hydrothermal synthesis [8–10] or by post-synthesis modifications [11–15]. Flanigen synthesized Ti-zeolites by post synthesis using ammonium fluorotitanate in solution [12]. But insufficient evidence was provided for Ti incorporation. Sayari et al. reported that incorporation of titanium into the framework of zeolite beta was achieved by simply treating Na-beta zeolite with an ammonium titanyloxalate solution [14]. Recently, Thomas et al. introduced a novel surface grafting methodology using titanocene dichloride that allows placement of atomically dispersed, tetrahedral titanium sites onto the inner walls of mesoporous MCM-41 [15].

The following examples pertain to zeolite modification by post-synthesis methods using $TiCl_4$ and catalytic properties. $TiCl_4$ vapor was applied to introduce Ti atoms into vacant framework positions of highly dealuminated ZSM-5 [11]. This titanium silicalite exhibited the same catalytic properties as hydrothermally synthesized TS-1 of high purity in the hydroxylation of phenol [16]. Ferrini and Kouwenhoven reported on the secondary synthesis of Ti-modified ZSM-5, beta and Y by reaction of $TiCl_4$ or Ti tetraisopropylate with H-zeolite samples [17]. Generally, tetrahedrally coordinated Ti in zeolite framework sites has been considered as an active site in selective oxidations [5,14,16]. Therefore, zeolite dealumination seemed essential for titanium incorporation into the zeolite framework before reaction with $TiCl_4$ [11]. However, exceptions exist. Ti grafted on to the surface of MCM-41 exhibited high catalytic performance in the epoxidation of cyclohexene [15]. Ti present on the external surface of silicalite is active in the hydroxylation of phenol with aqueous hydrogen peroxide [18].

In this work, Ti-ZSM-5 zeolites were prepared by reacting HZSM-5 with $TiCl_4$ vapor at elevated temperature, and were characterized by spectroscopic techniques such as skeletal and surface hydroxy FT-IR, XPS, and XANES. The catalysts were evaluated and compared by performing cyclohexanone ammoximation.

2. Experimental

The procedure for synthesis of Ti-ZSM-5 zeolites was similar to that reported in the literature [19]. HZSM-5 (SiO_2/Al_2O_3 ratios of 80, 50, and 30, respectively, PQ Corp.) was heated to 400 °C at a rate of 1 °C/min in a flow of dry N_2. The sample was then contacted with a flow of $TiCl_4/N_2$ for 2 h at 400 °C, and then the sample

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was flushed for 12 h with dry N_2 to remove physically adsorbed $TiCl_4$. The resulting catalyst was washed with distilled water and dried in air at 100 °C. TS-1 (Si/Ti = 23) was hydrothermally synthesized according to the method reported by Ratnasamy et al. [20]. Ti-loaded ZSM-5 materials prepared by ammonium titanyloxalate and Cp_2TiCl_2 were based on Sayari and Thomas methods, respectively [14,15]. Ti contents of Ti-ZSM-5 were determined by ICP-AES.

XRD was carried out on a Rigaku D/MAX-3B diffractometer using monochromatic Cu-Kα radiation. BET surface area was calculated from N_2 adsorption isotherms using a Micromeritics model ASAP 2400. FT-IR spectra were recorded on a Nicolet Magna-IR 560 spectrometer over the range of 600–4000 cm^{-1}. XANES spectra were obtained at the BL-3C facility of the Pohang light source of Pohang Accelerator Laboratory in Pohang (Korea) with a ring energy of 2.2 GeV and a stored current of 150–250 mA. XANES spectra were recorded in a transmission mode at room temperature with a Si(III) channel cut monochromator. Photon energy was calibrated by characteristic pre-edge peaks in the adsorption spectrum of a Ti foil (4964.2 eV). The X-ray photoelectron spectra were obtained using an ESCALAB MK II spectrometer provided with a hemispherical electron analyzer and a Mg anode X-ray exciting source (Mg Kα = 1253.6 eV). A binding energy of 284.6 eV for C_{1s} was chosen as the internal reference.

The catalytic tests were carried out in a three-necked glass flask fitted with a condenser and a rubber septum through which aqueous 30% H_2O_2 was injected dropwise over a period of 3 h using a feed pump. After 4 h reaction, the reaction mixture was extracted with diethyl ether and analyzed by GC (HP 5890 series II, capillary column HP1, FID detector).

3. Results and discussion

Figure 1(A) shows the comparative FT-IR skeletal spectra of HZSM-5(80) and Ti-ZSM-5(80), hereinafter the number in parentheses denotes the ratio of SiO_2/Al_2O_3, treated with different precursors, such as $TiCl_4$, ammonium titanyloxalate and Cp_2TiCl_2, respectively. For the purpose of determining accurate IR absorbance, we measured the spectra in the absorbance mode after the samples under vacuum, which can eliminate contamination of H_2O. All samples exhibit absorption bands at 803 cm^{-1} due to symmetric stretching of Si–O–Si and at 1106 and 1223 cm^{-1} due to asymmetric stretching of Si–O–Si [21]. The absorbance values were normalized with the 1106 cm^{-1} band that is assigned to the Si–O–Si asymmetric stretch of the zeolite framework. Ti-ZSM-5 prepared by $TiCl_4$ only exhibited an absorption band at 965 cm^{-1}. Although dispute still remains in the assignment of the band near 965 cm^{-1} for Ti-containing zeolites, this band has been generally assigned to –Ti=O with tetrahedral symmetry [22] or an asymmetric stretching mode of tetrahedral Si–O–Ti linkages [23] in the zeolite framework. Among the three different Ti precursors used in the preparation of Ti-ZSM-5, only $TiCl_4$ seems to be effective for incorporating Ti atoms into tetrahedral framework sites.

Hence, we chose $TiCl_4$ as a Ti source in the preparation of Ti-ZSM-5. Figure 1(B) shows FT-IR spectra of TS-1, ZSM-5, and Ti-ZSM-5 samples with SiO_2/Al_2O_3 ratios of 30, 50, and 80, respectively. A band at 965 cm^{-1} assigned as tetrahedral Ti in zeolite is observed in all cases for Ti-ZSM-5. The band intensity of 965 cm^{-1}grows with increasing SiO_2/Al_2O_3 ratio, indicating that Ti incorporation is easier with HZSM-5 containing higher amounts of

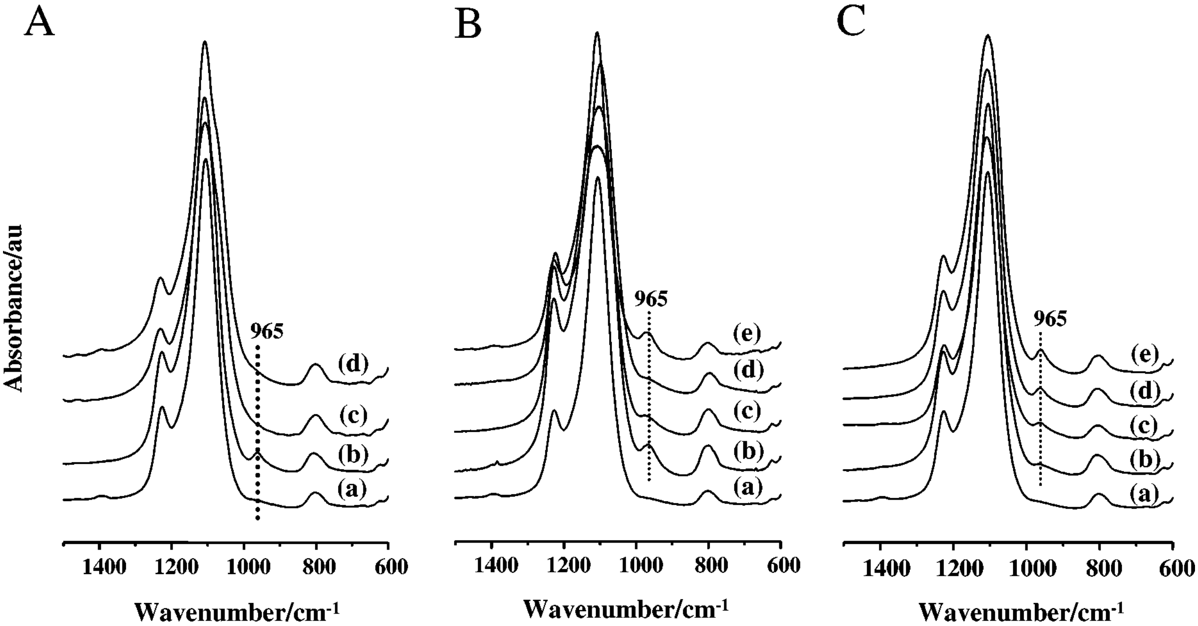

Figure 1. FT-IR skeletal spectra of HZSM-5 and Ti-ZSM-5(80): (A) with different precursors: (a) HZSM-5(80), (b) $TiCl_4$, (c) ammonium titanyloxalate, and (d) Cp_2TiCl_2; (B) with different SiO_2/Al_2O_3 ratios: (a) HZSM-5(80), (b) Ti-ZSM-5(80), (c) Ti-ZSM-5(50), (d) Ti-ZSM-5(30), and (e) TS-1; (C) at different temperatures: (a) no treatment, (b) 200 °C, (c) 300 °C, (d) 400 °C, and (e) 500 °C.

Table 1
Characterization results of HZSM-5 and Ti-ZSM-5 zeolites.

Sample	SiO_2/Al_2O_3	Surface area[a] (m^2/g)	Bulk Ti[b] (wt%)	Surface Ti (XPS)[c]	
				T_d	TiO_2
HZSM-5	80	462	–	–	–
Ti-ZSM-5(80)	80	443	2.6	68.9	31.1
Ti-ZSM-5(50)	50	452	0.9	27.1	3.5
Ti-ZSM-5(30)	30	453	0.8	22.8	1.9

[a] Determined by BET full isotherm.

[b] Determined by ICP-AES.

[c] Relative amounts of tetrahedral Ti and TiO_2, which were normalized to 100 based on Ti-ZSM-5(80).

SiO_2. For comparison, the FT-IR spectrum of TS-1 is also shown. Ti-ZSM-5(80) exhibits similar intensity of the band at 965 cm^{-1} compared to that of TS-1, which implies that the CVD method using $TiCl_4$ studied in this work can be achieved for preparing Ti-ZSM-5 zeolite comparable to TS-1 without any pretreatment such as dealumination.

For investigating the effect of CVD reaction temperature for Ti incorporation into HZSM-5, HZSM-5(80) was used as a parent sample. As shown in figure 1(C), the band intensity of 965 cm^{-1} increases as reaction temperature increases from 200 to 500 °C. The band intensity does not evolve higher than 400 °C, which can be considered an optimum temperature for the incorporation of Ti over HZSM-5. It seems that higher amounts of Ti can be incorporated into HZSM-5 at least at 400 °C.

The characteristics of HZSM-5 before and after $TiCl_4$ treatment are summarized in table 1. The XRD pattern (not shown) and BET data indicate that $TiCl_4$ treatment does not affect the zeolite structure and surface area remains unaltered within the limits of experimental error. Surface areas of Ti-ZSM-5(30), Ti-ZSM-5(50), and Ti-ZSM-5(80) are lowered by 2, 2, and 5% of that of HZSM-5, respectively. These results show that the CVD method attempted in this work does not damage the zeolite structure due to $TiCl_4$ treatment.

XPS provides important information about Ti species and their loading. Ti core level spectra of Ti-ZSM-5 are shown in figure 2. After background removal, the Ti_{2p} doublet was fitted with two sets of doublets which are centered at binding energies of 459.8 and 458.3 eV, respectively. The peak at 459.8 eV is closer in energy for tetrahedral Ti species and a small peak at 458.3 eV can be assigned as bulk TiO_2 [24]. As the SiO_2/Al_2O_3 ratio increases, the peak of $Ti_{2p_{3/2}}$ slightly shifts to lower binding energy, meaning that Ti-ZSM-5(80) contains a higher TiO_2 phase than that of Ti-ZSM-5(50) or Ti-ZSM-5(30), respectively. From the calculation of intensities, the $Ti_{2p_{3/2}}$ peak intensity of Ti-ZSM-5(80) is three times larger than that of Ti-ZSM-5(50) and Ti-ZSM-5(30), as indicated in table 1 and figure 2. This demonstrates that Ti-ZSM-5(80) contains Ti species of not only tetrahedral geometry but also a TiO_2 phase. On the other hand, Ti atoms in Ti-ZSM-5(50) and Ti-ZSM-5(30) are located mainly in tetrahedral sites.

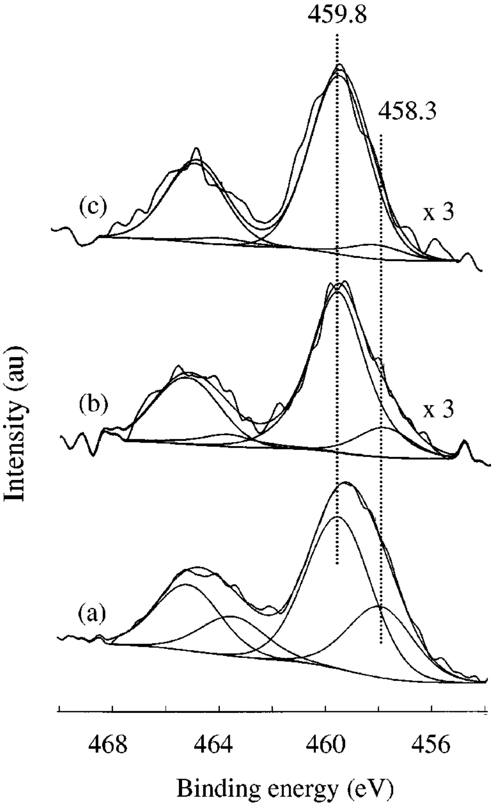

Figure 2. Deconvolution of XP Ti_{2p} spectra of (a) Ti-ZSM-5(80), (b) Ti-ZSM-5(50), and (c) Ti-ZSM-5(30).

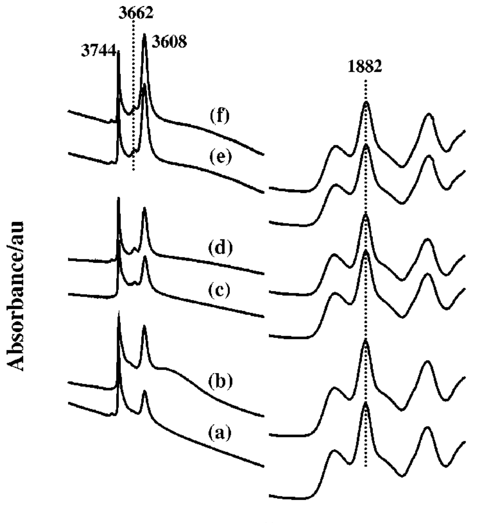

Figure 3. FT-IR spectra of HZSM-5 and Ti-ZSM-5 prepared by treatment with $TiCl_4$ at 400 °C: (a) Ti-ZSM-5(80), (b) HZSM-5(80), (c) Ti-ZSM-5(50), (d) HZSM-5(50), (e) Ti-ZSM-5(30), and (f) HZSM-5(30).

From FT-IR studies, we suggest that there is a reaction between $TiCl_4$ and hydroxyl groups of HZSM-5. Figure 3 shows the comparative FT-IR spectra in the hydroxyl stretching region for the parent HZSM-5 and Ti-ZSM-5 with various SiO_2/Al_2O_3 ratios. The FT-IR peak intensities were normalized with the 1882 cm^{-1} band which is assigned to the Si–O overtone of the zeolite framework [25]. HZSM-5 zeolites exhibit a band at 3744 cm^{-1} due to terminal silanol groups and a band at 3608 cm^{-1} attributed to structural Si(OH)Al groups [26]. A weak band at 3662 cm^{-1} is also detected, which is assigned to hydroxyl groups linked to aluminum atoms dislodged from the framework [27]. After treatment of HZSM-5 with $TiCl_4$ at 400 °C, only the band at 3608 cm^{-1} is considerably decreased in intensity as compared to that for HZSM-5 itself. However, no change in terminal silanol groups is observed. This result suggests that $TiCl_4$ has mainly reacted with the structural Si(OH)Al groups, where Ti atoms may be incorporated not into framework sites but into surface acidic hydroxyl groups. On the other hand, Kim et al. reported that all the FT-IR bands shift slightly toward the lower frequency region after treatment with $TiCl_4$, as compared to that of the dealuminated parent zeolite [28]. The substitution of Ti for Si in the zeolite framework results in an absorption band shift to a lower frequency region due to the longer Ti–O bond distance as compared with the Si–O bond. Zhanglin et al. successfully substituted Ti into ZSM-5 zeolite using an aqueous solution of $(NH_4)_2TiF_6$ resulting in an increase in the unit cell parameters of XRD and red shifts of symmetry and asymmetry stretching vibrational frequencies of zeolites in FT-IR [29]. Experimentally, we do not observe any shift to lower frequency after treatment with $TiCl_4$ in the skeletal FT-IR study. A decreasing trend of band intensity at 3608 cm^{-1} in terms of SiO_2/Al_2O_3 ratio agrees with the content of Ti located in tetrahedral sites analyzed by skeletal FT-IR and XPS. Actually it is difficult to distinguish the location of Ti sites between surface and framework by spectroscopic evidence such as skeletal FT-IR and XPS. From the hydroxy-FT-IR results investigated here, however, Ti atoms are mainly located in the zeolite surface having tetrahedral geometry.

Assuming that the bridged hydroxyls react with $TiCl_4$ to produce Ti-ZSM-5, based on FT-IR studies, the estimated maximum loadings of Ti atoms in Ti-ZSM-5(30), Ti-ZSM-5(50) and Ti-ZSM-5(80) are 4.6, 2.7, and 1.7 wt%, respectively. This is contradictory to experimental results shown in table 1. Probably this is due to the fact that hydrophobic $TiCl_4$ molecules more readily react with higher hydrophobic HZSM-5(80) than less hydrophobic HZSM-5(30).

Other evidence of tetrahedrally coordinated Ti atoms on zeolite surfaces is demonstrated in figure 4, showing the Ti K-edge spectra of TS-1 and Ti-ZSM-5(80). The preedge peaks of Ti-ZSM-5(50) and Ti-ZSM-5(30) containing less than 1 wt% Ti, respectively, were not shown because the intensities are too weak. The preedge peaks in the XANES region are ascribed to 1s → 3d transitions of the excited electron and contain information about the coordination environment of the absorbing Ti atom. The Ti-ZSM-5(80) catalyst exhibits a single preedge peak, which is assigned to tetrahedrally coordinated Ti on the surface of ZSM-5. The preedge is detected by the very few genuine tetrahedral and quasi-tetrahedral Ti species known in the literature [30]. This observation is in good agreement with the report by Anpo and coworkers [31]. They observed intense peaks on the surface of tetrahedrally coordinated titanium oxide anchored onto Vycor glass.

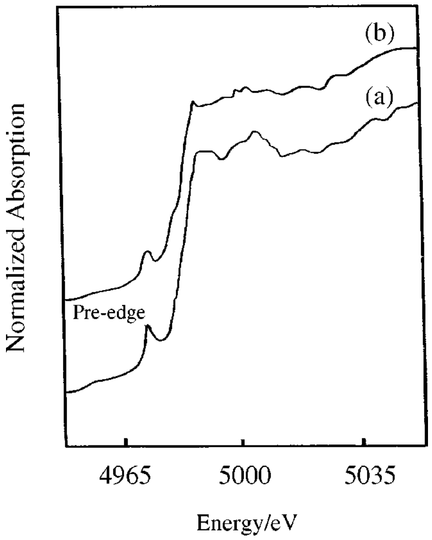

Figure 4. Ti K-edge XANES spectra of (a) TS-1 and (b) Ti-ZSM-5(80).

Table 2
Ammoximation of cyclohexanone over various catalysts.[a]

Catalyst	Conv.[b] (%)	Sel.[c] (%)
HZSM-5(80)	0.8	3.2
Ti-ZSM-5(80)	88.6	69.6
Ti-ZSM-5(50)	65.2	89.4
Ti-ZSM-5(30)	61.7	91.3
TS-1 (Si/Ti = 23)	88.2	82.7

[a] Conditions: catalyst 1 g, cyclohexanone 0.1 mol, cyclohexanone : $NH_4OH : H_2O_2 = 1 : 1.5 : 1$, reaction run 4 h, temperature 60 °C.
[b] Conv. = cyclohexanone conversion.
[c] Sel. = cyclohexanone oxime selectivity among the products.

We have attempted cyclohexanone ammoximation for the evaluation of catalytic properties of the Ti-ZSM-5 samples. The results obtained are summarized in table 2. For comparison, TS-1 was also tested. The major product is found to be cyclohexanone oxime, together with small amounts of ε-caprolactam and peroxydicyclohexylamine. All Ti-ZSM-5 catalysts show activity in the ammoximation. However, HZSM-5(80) possesses very little conversion, less than 1%. The catalytic conversion increased in the following order:

$$\text{Ti-ZSM-5(80)} \geqslant \text{TS-1} > \text{Ti-ZSM-5(50)} > \text{Ti-ZSM-5(30)}.$$

With increasing SiO_2/Al_2O_3 ratio in Ti-ZSM-5, the conversion is enhanced. To understand why Ti-ZSM-5 with high SiO_2/Al_2O_3 ratios gives higher conversion, we correlate the conversion to previous spectroscopic data for Ti. From such characterization, the conversion is proportional to highly dispersed titanium loadings, especially tetrahedral site in the surface, suggesting that tetrahedral Ti in zeolite surfaces seems to be the active site. The selectivity to oxime shows an inverse trend compared to conversion:

$$\text{Ti-ZSM-5(30)} > \text{Ti-ZSM-5(50)} > \text{TS-1} > \text{Ti-ZSM-5(80)}.$$

Ti-ZSM-5(30) with tetrahedral Ti is found to have a higher selectivity to oxime than Ti-ZSM-5(80) not having only tetrahedral Ti but also considerable extraframework Ti. This phenomenon was also observed in phenol hydroxylation over titanium silicalite, suggesting that the selectivity to hydroquinone and catechol is strongly affected by the presence of TiO_2 amounts [16]. That is, the selectivity is also proportional to the content of tetrahedral Ti.

4. Conclusions

Based on spectroscopic investigations and catalytic performance over Ti-ZSM-5 prepared in this work, the following conclusions may be drawn:

(1) $TiCl_4$ treatment does not affect the HZSM-5 zeolite structure during the synthesis of Ti-ZSM-5 and surface area remains unaltered.

(2) Among the representative precursors, $TiCl_4$, ammonium titanyloxalate, and Cp_2TiCl_2, only $TiCl_4$ is effective in making Ti-ZSM-5 zeolite.

(3) Content of incorporated Ti in Ti-ZSM-5 zeolite increases on increasing the SiO_2/Al_2O_3 ratio, indicating that hydrophobic ZSM-5 is more effective for the incorporation of Ti. $TiCl_4$ treatment temperature of 400–500 °C is optimal.

(4) Ti atoms react with hydroxyl groups of structural Si(OH)Al, which are located in the zeolite surface having tetrahedral geometry from characterization via skeletal- and surface hydroxy-FT-IR, XPS, and XANES spectroscopic studies.

(5) Ti-ZSM-5 prepared by $TiCl_4$ is an active catalyst with considerable conversion and selectivity compared to TS-1 in cyclohexanone ammoximation. Tetrahedrally coordinated Ti atom exists in the zeolite surface and is proposed as an active site.

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