

## Incorporation of Titanium into H-ZSM-5 Zeolite via Chemical Vapor Deposition: Effect of Steam Treatment

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Ti-ZSM-5 prepared by secondary synthesis, from the reaction of H-ZSM-5 with vapor phase  $\text{TiCl}_4$ , was characterized with several physicochemical techniques including FT-IR and UV/VIS-DRS. It was found that zeolite structure, surface area and pore volume did not change, and the framework aluminum could not be replaced by titanium atom during the secondary synthesis of Ti-ZSM-5. The incorporation of titanium into the framework might be due to reaction of  $\text{TiCl}_4$  with the silanol groups associated with defects or surface sites. The formation of extra-framework titanium could not be avoided, unless the samples were further treated by water vapor at 550 °C or higher temperature. High temperature steam treatment of Ti-ZSM-5 prepared by chemical vapor deposition with  $\text{TiCl}_4$  was efficient to prevent the formation of non-framework titanium species. Ti-ZSM-5 zeolites prepared in this work contained only framework titanium species and exhibited improved catalytic property close to TS-1 prepared by hydrothermal synthesis.

**Key Words :** TS-1,  $\text{TiCl}_4$ , Secondary synthesis, Water vapor, Styrene oxidation

### Introduction

TS-1 with MFI structure was firstly synthesized by Taramasso and coworkers<sup>1</sup> in 1983, and the TS-1 has tetrahedral titanium atoms incorporated in the framework of zeolites. Since then, various kinds of Ti-containing molecular sieves have been studied by many researchers because of their interesting catalytic properties.<sup>1-6</sup> TS-1 has been used in various oxidations including epoxidations.<sup>7,8</sup>

Hydrothermal synthesis<sup>9-11</sup> and post-synthesis<sup>12,13</sup> are the two main pathways for the preparation of Ti-containing molecular sieves. The post-synthesis is accomplished with a vapor phase treatment of zeolites with  $\text{TiCl}_4$ , which is also mentioned as gas-solid phase isomorphous substitution with  $\text{TiCl}_4$ <sup>6</sup> or as CVD method.<sup>14</sup>

As is well known, the active site of Ti-containing molecular sieves in many selective oxidations of various organic compounds (using mainly dilute  $\text{H}_2\text{O}_2$  as an oxidant) is framework titanium in tetrahedral coordination, and the presence of extra-framework titanium is known to lead to the decomposition of  $\text{H}_2\text{O}_2$ , resulting in the decrease of the efficiency of  $\text{H}_2\text{O}_2$ . But it is difficult to obtain zeolites containing only framework titanium from the reaction with  $\text{TiCl}_4$ .<sup>6,14-16</sup>

In the present work, Ti-ZSM-5 prepared from vapor phase treatment of H-ZSM-5 with  $\text{TiCl}_4$  has been characterized by XRD, XPS, FT-IR, UV-DRS and styrene epoxidation reaction. The effects of aluminum content, flushing with

nitrogen and treatment with water vapor at high temperature on the post-synthesis of Ti-ZSM-5 are described.

### Experimental Section

**Treatment of H-ZSM-5 with  $\text{TiCl}_4$  and water vapor.** Calcined H-ZSM-5 (5 g) was loaded into a quartz reactor and heated to 500 °C for 2 h in a flow of dry nitrogen to remove moisture. The dehydrated samples were then exposed to a flow (65 mL/min) of dry nitrogen bubbled through a vessel containing  $\text{TiCl}_4$  maintained at room temperature. After the  $\text{TiCl}_4$  treatment for a predetermined time and temperature, the dry nitrogen flow without  $\text{TiCl}_4$  was continued to remove physisorbed  $\text{TiCl}_4$  for 2 h at a fixed temperature. After the treatment with  $\text{TiCl}_4$  and flushing with nitrogen, the zeolite was contacted with water vapor. The samples containing titanium species were treated at 550 °C for 3 h with nitrogen stream that passed a bubbler containing water at 70 °C.

The resulting catalysts (both the  $\text{TiCl}_4$  treated and water vapor treated) were washed with distilled water and dried in air at 100 °C.

**Characterization.** FT-IR spectra were recorded with a Nicolet 200SXV spectrometer in the range of 400-2000  $\text{cm}^{-1}$ . The X-ray powder diffraction (XRD) patterns were obtained with a RigakuD/MAX- $\gamma$ A powder diffractometer using  $\text{Cu K}\alpha$  radiation. The x-ray-photoelectron spectra were obtained with a NP-1X X-ray photoelectron spectrometer using  $\text{Mg K}\alpha$  radiation. The binding energy of C1s (284.6 eV) was used as an internal reference. Diffuse reflectance UV/VIS spectra were recorded using a Hitachi UV-340 spectrometer equipped with a diffuse reflectance attachment, and  $\text{BaSO}_4$

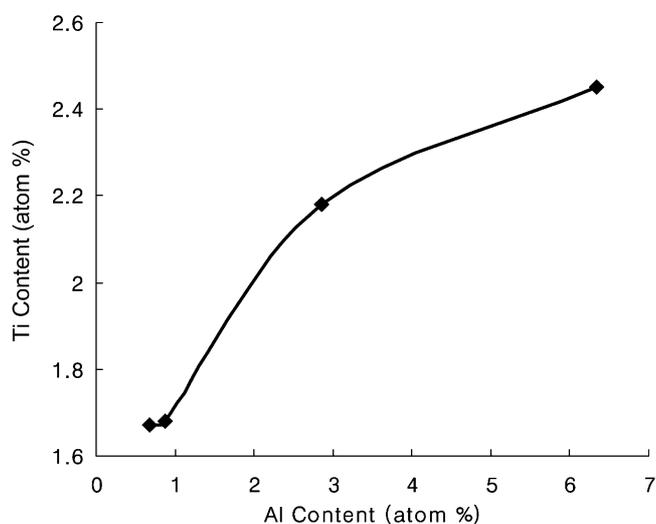
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was used as a reference. BET surface area was calculated by analyzing  $N_2$  adsorption isotherms obtained with Digisorb 2600. Titanium and aluminum contents of the Ti-ZSM-5 were analyzed by an ICP, and the concentrations were reported as atom % based on the total metal atoms such as Al, Si and Ti.

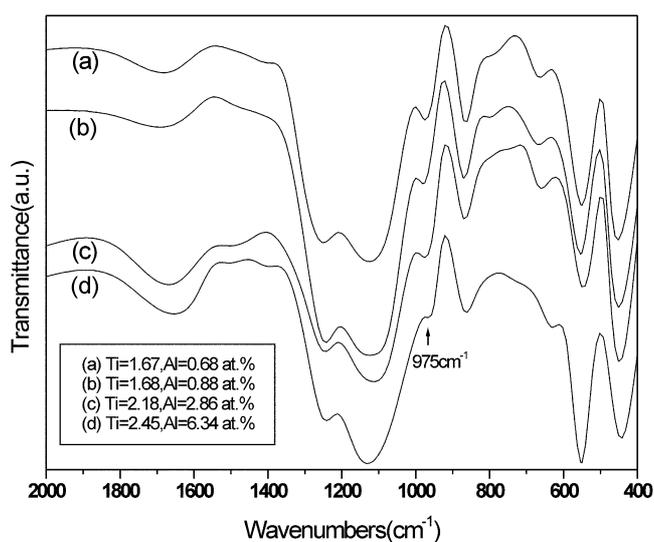
**Epoxidation of styrene.** Styrene epoxidation was carried out in a glass flask (50 mL) equipped with a reflux condenser, a magnetic stirrer, a thermometer and a septum to withdraw samples periodically for analysis. Catalyst of 0.35 g, 12 mL acetone as solvent, 34.9 mmol of styrene (99%, Aldrich) and 1.3 mL aqueous hydrogen peroxide solution (30wt.%) were loaded into the flask. The reaction was performed for 6 h at 70 °C. The liquid mixture was separated from catalyst, and analyzed using a gas chromatography (SC-1001) fitted with a flame ionization detector and a capillary column (Supelco PTE<sup>TM</sup>-5). Every peak was identified with authentic molecules. The conversion and selectivity of styrene epoxide were calculated from the concentrations of styrene remained and styrene oxide produced, respectively. The conversion was mole% of the maximum styrene conversion expected by the concentration of  $H_2O_2$ . So, 100% conversion corresponds to the 25% conversion of styrene when the styrene/ $H_2O_2$  molar ratio in the reaction mixture was 4.

## Results and Discussion

**Effect of aluminum content of ZSM-5 on  $TiCl_4$  treatment.** The titanium content of the  $TiCl_4$  treated samples increases with increasing framework aluminum concentration as shown in Figure 1, indicating that aluminum or acid sites due to the framework aluminum may contribute to the adsorption of titanium species on zeolites. The amount of framework titanium rather than extra-framework titanium is important because the extra-framework titanium can promote decomposition of hydrogen peroxide to dioxygen



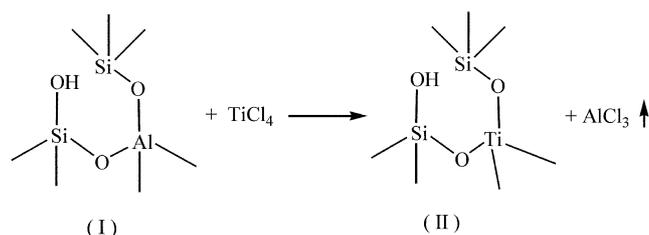
**Figure 1.** Titanium contents of Ti-ZSM-5 with aluminum content of parent H-ZSM-5 zeolites. The zeolites were treated with  $TiCl_4$  for 2 h and flushed with nitrogen for 2 h at 500 °C.



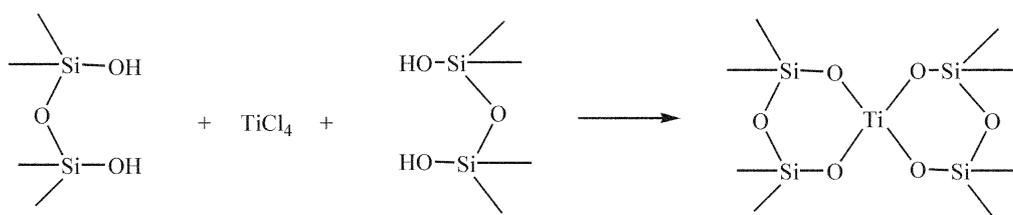
**Figure 2.** FT-IR spectra of H-ZSM-5 treated with  $TiCl_4$ . The zeolites were treated with  $TiCl_4$  for 2 h and flushed for 2 h at 500 °C. The parent H-ZSM-5 zeolites have different aluminum concentrations and the treated zeolites have different titanium contents. The Al and Ti concentrations are atom % based on (Al+Si+Ti).

and water in oxidation of organic compounds. FT-IR spectrum of typical TS-1 show an intense band at  $\sim 975\text{ cm}^{-1}$ , which is a characteristic band of an isolated framework titanium.<sup>17-19</sup> The low intensity of this band in the treated sample (Figure 2) may indicate that most of titanium species exist in extra-framework sites. From UV/VIS-DRS, it can also be understood that most of the titanium exist in octahedral or polymeric  $TiO_2$  states (Spectra not shown). Moreover, the framework tetrahedral titanium decreases with increasing titanium or aluminum content as presented in Figure 2. This may show that the aluminum in ZSM-5 can prevent incorporation of titanium in the framework of zeolites. We had reported that the incorporated titanium increased with increasing Si/Al ratio due to increased hydrophobicity of a zeolite.<sup>14</sup>

It has generally been agreed that titanium substitutes the boron site in molecular sieves containing boron during secondary synthesis with  $TiCl_4$ .<sup>16,20-22</sup> Therefore, a similar mechanism to replace aluminum with titanium can be assumed during the reaction of ZSM-5 with  $TiCl_4$  (Scheme 1). However, in this work, no decrease in aluminum content was observed after H-ZSM-5 was treated with  $TiCl_4$ . Therefore, the incorporation of titanium in the framework of



**Scheme 1.** Mechanism of direct replacement of framework aluminum with titanium.

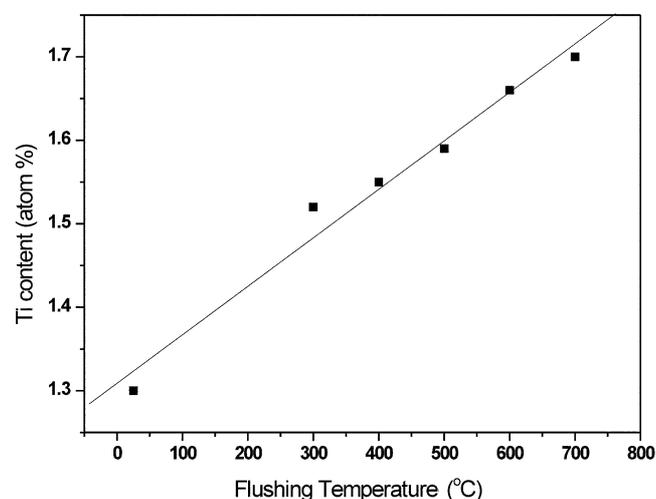


**Scheme 2.** Mechanism of titanium insertion through the reaction of  $\text{TiCl}_4$  with silanol groups associated with defect sites.<sup>17</sup>

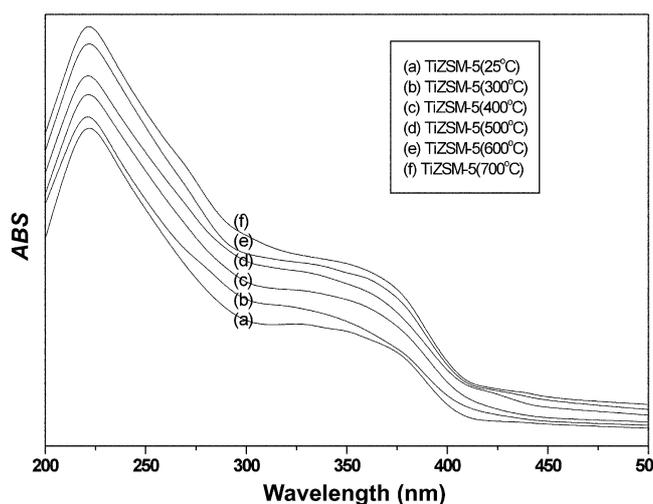
ZSM-5 (even in small quantity) may occur from the reaction of  $\text{TiCl}_4$  with silanol groups associated with defects or surface sites (Scheme 2). Similar mechanisms are quite well documented by several research groups.<sup>17</sup> Isomorphous substitution of silicon or aluminum with titanium probably does not occur.

**Effect of flushing temperature.** When Ti-ZSM-5 is produced by  $\text{TiCl}_4$  treatment in vapor phase,  $\text{TiCl}_4$  molecule physisorbed on the surface of zeolites should be flushed completely because the residual  $\text{TiCl}_4$  may be transformed to  $\text{TiO}_2$  or extra-framework titanium species during washing or contacting with humid air. Flushing temperature is also important because residual  $\text{TiCl}_4$  molecules will be removed quickly at high temperature. However, physisorbed  $\text{TiCl}_4$  may further react with H-ZSM-5 at high temperature to affect the titanium content. As shown in Figure 3, the titanium content increases linearly with increasing the flushing temperature. This may represent that high temperature flushing causes titanium species to interact strongly to the ZSM-5 not to be removed by washing with water.

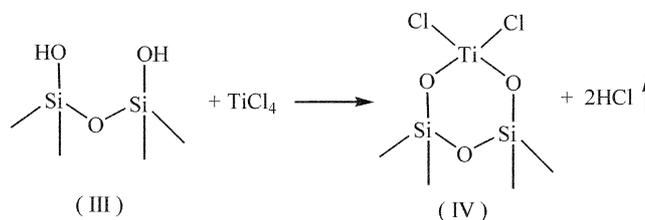
The UV/VIS-DRS spectra of all zeolites (Figure 4) show intense absorption maxima at  $\sim 220$  nm, which can be assigned to an isolated titanium with tetrahedral coordination. Another absorption edge found in the range of 300–380 nm indicates that some titanium are also in an octahedral environment. All of the samples that have been exposed to air after flushing with nitrogen always produced two kinds of titanium species (Figure 4), even after long



**Figure 3.** Titanium contents with the flushing (2 h) temperature of H-ZSM-5 (Al = 0.68 atom %) treated with  $\text{TiCl}_4$  for 2 h at 500 °C.



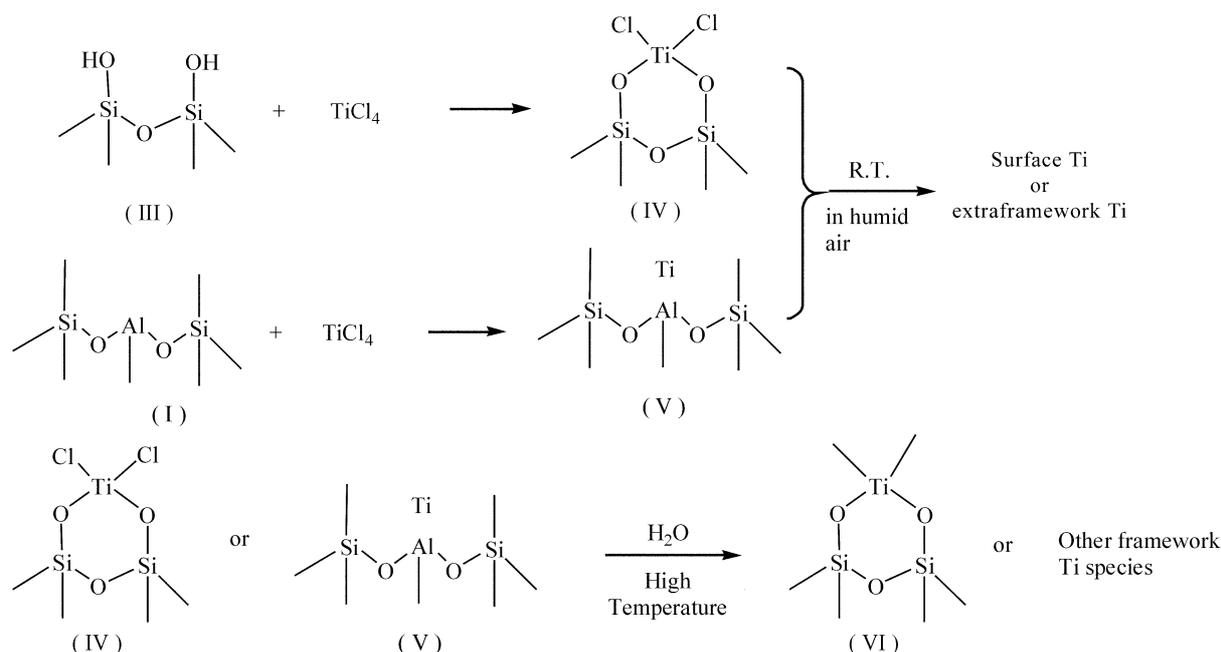
**Figure 4.** UV/VIS-DRS spectra of Ti-ZSM-5 (Al = 0.68 atom %) prepared from different flushing temperatures.



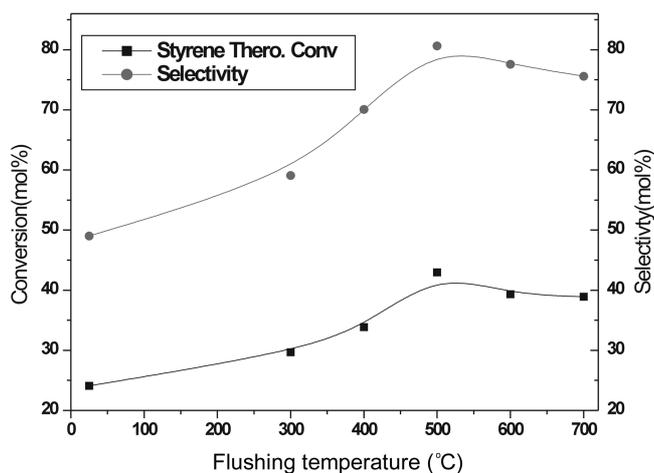
**Scheme 3.** Mechanism of titanium insertion through the reaction of  $\text{TiCl}_4$  with silanol groups associated with surface sites.<sup>16</sup>

flushing time. This may be due to the intermediate, structure IV (Scheme 3), formed from the reaction between  $\text{TiCl}_4$  and two silanol groups on surface sites of zeolites.<sup>16</sup> This structure IV is not stable in humid air at low temperature, and can be transformed into extra-framework titanium species as shown in Scheme 4.

The styrene oxidation results of Figure 5 show that activity and selectivity of Ti-ZSM-5 increase with the increasing flushing temperature below 500 °C. This increased activity and selectivity may be due to the increased tetrahedral framework titanium in Ti-ZSM5 as reported earlier. However, when the flushing temperature is higher than 500 °C, catalytic performances decrease slightly with increasing flushing temperature, even though titanium content increases further (Figures 3 and 5). This result may be due to the fact that two adjacent  $\text{TiO}_4$  groups (for example,  $-\text{Si}-\text{O}-\text{Ti}-\text{O}-\text{Ti}-\text{O}-\text{Si}-$ ) can be formed on the surface of zeolites under very



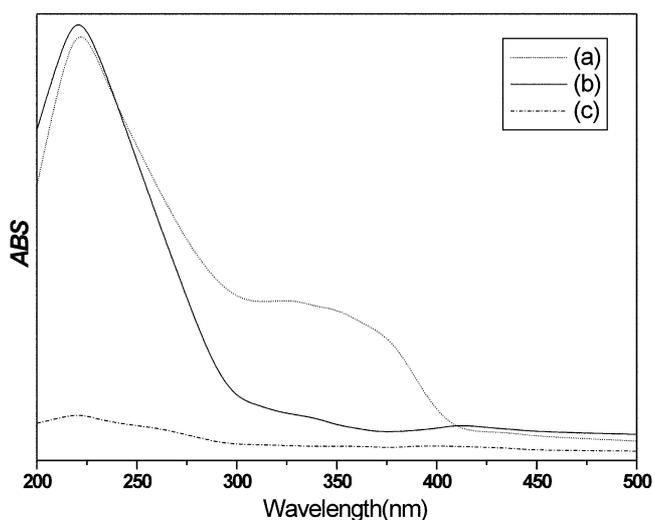
**Scheme 4.** Mechanism of interactions of water vapor with surface of a  $\text{TiCl}_4$  treated zeolite under different temperatures.



**Figure 5.** Epoxidation of styrene over Ti-ZSM-5 (Al = 0.68 atom %) prepared from different flushing temperatures. Before the flushing, the H-ZSM-5 was treated with  $\text{TiCl}_4$  for 2 h at 500 °C.

high temperature due to the increased Ti concentration. This adjacent  $\text{TiO}_4$  groups may decrease selectivity of oxidation because of the decomposition of  $\text{H}_2\text{O}_2$ .<sup>23</sup> On the other hand, the decreased performances of the catalysts flushed at 600–700 °C may be related with the increased non-framework Ti species. Therefore it is necessary to develop suitable preparation methods of Ti-ZSM-5 without any extra-framework titanium species.

**Treatment with high temperature steam.** UV/VIS-DRS spectra of zeolites (that are treated by steam at 550 °C for 3 h after flushing for 2 h at 500 °C) show only an intense absorption band at ~220 nm (Figure 6), which is assigned to an isolated tetrahedral  $\text{TiO}_4$  unit. The results of chemical analysis and XPS for H-ZSM-5 and two types of Ti-ZSM-5 (just flushed, and flushed and steam treated) are summarized



**Figure 6.** UV-DRS spectra of various ZSM-5 samples. (a)  $\text{TiCl}_4$  treated for 2 h at 700 °C and flushed for 2 h with nitrogen at 500 °C. (b)  $\text{TiCl}_4$  treated for 2 h at 700 °C, flushed for 2 h with nitrogen at 500 °C and treated with water vapor ( $P = 31.2$  kPa) for 3 h at 550 °C. (c) Parent H-ZSM-5.

**Table 1.** Elemental analysis and binding energy of Ti 2p of Ti-ZSM-5 catalysts

Samples	Composition		Binding energy	
	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{TiO}_2}$	Ti 2p <sub>1/2</sub>	Ti 2p <sub>3/2</sub>
HZSM-5	244	—	—	—
TiZSM-5(a) <sup>a</sup>	248	53	464.7 466.2	459.0 460.4
TiZSM-5(b) <sup>b</sup>	252	54	466.1	460.3

<sup>a</sup>Treated with  $\text{TiCl}_4$  for 12 h at 500 °C, flushed for 2 h at 500 °C. <sup>b</sup>Treated with  $\text{TiCl}_4$  for 12 h at 500 °C, flushed for 2 h at 500 °C, treated by water vapor (steam pressure: 31.2 kPa) at 550 °C for 3 h.

**Table 2.** Styrene epoxidation over Ti-ZSM-5 catalysts

Catalyst	Styrene Conversion, % <sup>a</sup>	Distribution of products (mol%)		
		Benzaldehyde	Phenylacetaldehyde and styrene oxide	Others <sup>b</sup>
TiZSM-5(a) <sup>c</sup>	55.9	15.7	82.2	2.1
TiZSM-5(b) <sup>d</sup>	70.6	6.4	92.5	1.1
TS-1 <sup>e</sup>	76.8	16.1	82.0	1.9

<sup>a</sup>Conversion of styrene compared to the maximum expected conversion based on H<sub>2</sub>O<sub>2</sub>. <sup>b</sup>Styrenediol and some unidentified high boiling compounds. <sup>c,d</sup>Refer to Table 1. <sup>e</sup>Data from reference 1.

in Table 1. The XPS spectrum of the zeolite treated with TiCl<sub>4</sub> and flushed with nitrogen shows a peak composed of Ti 2p<sub>3/2</sub> doublets with binding energy of 460.4 eV and 459.0 eV (Table 1) (spectra not shown). The high and low binding energy can be assigned to the tetrahedral titanium species and amorphous TiO<sub>2</sub> particles, respectively, as has been reported by us.<sup>14</sup> However, the zeolite further treated with water vapor at high temperature has only one type of titanium species (Tetrahedral Ti, binding energy = 460.3 eV), suggesting that steam treatment may prevent the formation of extra-framework titanium species. The structure IV of scheme 3 is unstable at room temperature and can be easily transformed to extra-framework titanium species on the surface of zeolites (Scheme 4) as mentioned earlier. However, if water vapor is added to the zeolite at high temperature, silanol groups may form around the structure IV, and silanol groups may interact with Ti species of structure IV to further produce framework titanium species (Scheme 4). In other words, the titanium species adsorbed on the zeolite may be converted to framework titanium through the rearrangement of bonds via the treatment with water vapor at high temperature. Therefore, the treatment with water vapor at high temperature may prevent the formation of extra-framework titanium species. The XRD pattern and BET data (not shown) indicate that the zeolite structure and surface area do not depend significantly on the treatment conditions.

The Ti-ZSM-5 treated further with steam has demonstrated higher activity and selectivity in the styrene epoxidation as shown in Table 2. This increased activity and selectivity can be explained as a consequence of the increased framework titanium due to the steam treatment at high temperature. The treatment of TiCl<sub>4</sub>-contacted H-ZSM-5 with steam at high temperature prevents the formation of extra-framework or polymeric titanium species, and the activity and selectivity of epoxidation over the zeolites prepared in this study are close to those over TS-1 synthesized hydrothermally as presented in Table 2. Further work is necessary to understand the slight difference in conversion and selectivity with catalysts even though this may be related with the aluminum of ZSM-5 and titanium species.

### Conclusions

Based on the spectroscopic and catalytic results for the Ti-ZSM-5 prepared in this work, the following conclusions can

be drawn:

1) The direct replacement of framework aluminum with titanium does not occur during the vapor phase treatment of H-ZSM-5 with TiCl<sub>4</sub>, implying that the framework aluminum species prevents the incorporation of titanium ion with tetrahedral coordination in the framework of zeolites.

2) High temperature steam treatment of Ti-ZSM-5 prepared by chemical vapor deposition of TiCl<sub>4</sub> onto H-ZSM-5 was efficient to prevent the formation of extra-framework or polymeric titanium species. Ti-ZSM-5 zeolites prepared in this work exhibited improved catalytic property close to TS-1 prepared by hydrothermal synthesis.

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