The State of Ti in Titanoaluminosilicates Isomorphous with Zeolite β

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Abstract: A large-pore Ti-containing zeolite, which is active for hydrocarbon oxidation at mild conditions, has been obtained by direct synthesis. This is isomorphous with zeolite β, and the crucial effect of alkali metal cations on the product has been described. By means of IR spectroscopy, XRD, thermal analysis, XPS, EXAFS-XANES, and DRS-UV techniques, it has been shown that the synthesis carried out without alkali metal cations leads to zeolite β with Ti located in the framework positions. The results allow us to propose a model which explains the varying Ti coordination for as-made and calcined samples, hydrated and dehydrated. The model is consistent with the literature data on TS-1 and TS-2 structures.

Introduction

The isomorphous substitution of Si by Ti into the zeolite framework provides useful catalysts for the oxidation of organic compounds under mild conditions.[1-4] Till now only medium-pore-size zeolites have been used.[5-7] Zeolites TS-1 and TS-2 with the MFI and MEL structures, respectively, show good activity and selectivity in the oxidations of phenol to cathecol and hydroquinone,[1,6] olefins to epoxides,[1] and alkanes to alcohols and ketones[2,3,4] using H_2O_2 at relatively low temperatures (0–100 °C). The active sites are located inside zeolite pores, and their accessibility to reactant molecules, and therefore catalyst activity and selectivity, depends on the diameter of the zeolite channels. For TS-1 and TS-2 it has been reported[8] that only molecules with size ≤ 5.5 Å can effectively react. It should be possible to overcome this limitation and improve the performance of Ti-zeolite catalysts by the synthesis of novel large-pore structures.

A 12-membered-ring zeolite belonging to this category is zeolite β. The synthesis of Ti-containing zeolite β has been reported very recently,[9,10] and some characterization has already been done.[10] To summarize, for the Ti-β samples synthesized without alkali metal cations, a continuous increase of the interplanar *d*-spacing corresponding to the most intense XRD peak with the Ti content is observed.[9] These samples present an IR band at $\sim$960 m^{-1}, its intensity increasing with the Ti content. On the basis of the IR studies on as-made and calcined material, we have proposed that the band at $\sim$960 cm^{-1} present in Ti-β can be due to the Si–O stretching vibration in the Si–OR group, R being H^+ in the calcined state and TEA^+ in the as-made material.[11] Thermal analysis of the samples provides further support to this hypothesis, and the presence of Ti in a distorted –5 or –6 coordination in the zeolite as made is proposed to account for the IR and thermal analysis results.[10] However, the actual coordination of Ti in the as-made and calcined materials remains to be proved. The aim of this paper is to give some insight into the coordination state of Ti in Ti-β samples, which is crucial for proper understanding of the catalyst structure and the catalytic mechanism of the selective oxidation of organic compounds.

Table I. Chemical Composition of the Solids Synthesized from Akali-Free Reaction Mixtures

	composition of solid			
sample	Al/uc	Ti/uc	Ti/(Ti + Si)	T^{IV}/Al
1[a]	1.17	2.98	0.047	54
2	1.16	1.00	0.016	54
3	1.20	1.27	0.020	52
4	1.39	1.39	0.022	45
5	1.20	2.01	0.032	52
6	0.74	2.41	0.038	84
7	0.58	1.51	0.024	108

[a] Sample prepared in the presence of alkali cations (content: 3.63 Na_2O, 3.23 K_2O, wt %).

Experimental Section

Synthesis. Crystallizations were carried out at 408 ± 1 K in PTFE-lined stainless-steel 60-mL autoclaves stirred at 60 rpm. The following chemicals were used as reagents: amorphous silica (Aerosil 200, Degussa), titanium(IV) tetraethoxide (Alfa), tetraethylammonium hydroxide (40% aqueous solution, K < 1 ppm, Na < 3 ppm, Alfa), sodium aluminate (56% Al_2O_3, 38% Na_2O, Carlo Erba), aluminium nitrate nonahydrate (95% Merck), sodium hydroxide (98%, Prolabo), sodium chloride (99%, Prolabo), and potassium chloride (99.5%, Scharlau).

Molar composition of gels used for the synthesis was as follows:

$$x(0.33\ \mathrm{K},\ 0.67\ \mathrm{Na})_2\mathrm{O}{:}\mathrm{Al_2O_3}{:}u[y\mathrm{Ti},\ (1-y)\mathrm{Si}]\mathrm{O_2}{:}15u\mathrm{H_2O}{::}v\mathrm{TEA_2O}{:}z\mathrm{HCl}$$

where $H_2O/T^{IV}O_2 = 15$ and $(OH–2Al_2O_3)/T^{IV}O_2 = 0.52$ (see Table I for details).

The gels were prepared by the hydrolysis of Ti(IV) tetraethoxide in a solution containing tetraethylammonium cations followed by the hydrolysis of Aerosil in the resultant clear solution. Finally, alkaline solutions containing Al^{3+} and, optionally, $Na^+ + K^+$ were added to the mixture.

After cooling of the autoclaves, the samples were centrifuged at 10.000 rpm and the recovered solids were washed, until pH ≈ 9 was obtained, and then dried at 350 K. After each run, the PTFE liners were washed with HF (aq) to prevent accidental seeding. Chemical compositions of the samples studied in this work are given in Table I. Samples were calcined at 853 K in air for 3 h. In order to study sample **5** in the

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dehydrated state, by X-ray absorption spectroscopy a portion of this was heated under vacuum (10^{-4} Torr) at 573 K for 3 h.

A sample of TS-1 (Euro TS-1) containing 1.7 wt % of TiO_2 was used as a reference.

Characterization. X-ray powder diffraction patterns were recorded using Cu Kα radiation with a Philips PW 1830 diffractometer equipped with a graphite monochromator.

The crystallinity of the solids was determined by measuring the peak area at $2\theta \approx 22.4°$. The position of this peak was accurately measured after dehydration of the samples for 1 h at 383 K and further rehydration over a $CaCl_2$ saturated solution (35% relative humidity) for 16 h using Si as internal standard. X-ray fluorescence (Outokumpu X-MET 840) was used to determine the amount of Ti in the samples. Concentrations of Al and alkali metal cations were determined by atomic absorption (Perkin-Elmer 403) and flame emission spectroscopy (Ependorf ELEX 6361), respectively. Chemical analysis of the crystal surface was determined by X-ray photoelectron spectroscopy (XPS) with an ESCALAB-210 spectrometer. Binding energies were corrected for charge effects by referencing to the carbon 1s peak at 284.9 eV in the calcined samples and Si (2p) at 103.2 eV in the as-synthesized samples.

Diffuse reflectance spectra in the 190–800-nm range were recorded with a Shimadzu UV-2101 PC spectrophotometer equipped with a diffuse reflectance attachment using $BaSO_4$ as a reference.

The X-ray absorption spectra were recorded using synchrotron radiation provided by LURE (Orsay). The X-ray beam was emitted by the DCI storage ring running at 1.85 GeV with an average intensity of about 150 mA. The Ti *K*-edge spectra were recorded at room temperature using the XAS-III station.[12] X-rays were monocromatized using a Si (111) and a Si (311) two-crystal spectrometer for EXAFS and XANES, respectively. A special chamber was used to acquire data under vacuum for calcined dehydrated sample **5**. Experimental data were analyzed with a chain of programs developed by Michalowicz.[13]

All the XANES spectra were treated in a traditional way: from the experimental spectrum a linear background determined by least square fitting of the pre-edge experimental points was subtracted. The first inflection point of the spectrum obtained for a foil of titanium metal was used as energy reference. The spectra were normalized with respect to the beginning of the EXAFS oscillations around 45 eV above the absorption edge.

The standard procedures for background removal, extraction of EXAFS signal, and normalization of the edge absorption were applied.[14] The radial distribution functions were obtained by K^3-weighted Fourier transformation of the EXAFS data. A Kaiser window function, minimizing the side-lobes effects, was used to analyze the first coordination shell. The Fourier transform was calculated between 2.63 and 9.50 Å^{-1}, and the filtering of the first peak was carried out between 0.86 and 1.81 Å. We have used the EXAFS spectrum of a $SrTiO_3$ single crystal as a reference for the calculation of phase-shift function and backscattering amplitude for Ti–O, since in this oxide Ti is surrounded by six oxygen atoms at a unique distance (1.953 Å).[15] To study the second coordination sphere of titanium, a Hamming window in a larger range of *K* (2.96–11.00 Å^{-1}) was used in order to enhance the resolution of different peaks. The second peak of the Fourier transform was filtered out between 2.50 and 3.10 Å. Since it was not possible to find an appropriate compound to extract the phase-shift and backscattering amplitude for Ti–Si, we used the theoretical functions calculated by McKale.[16]

Catalytic Experiments. The catalytic experiments were carried out in a glass flask with reflux under stirring. The flask was heated by means of a temperature-controlled oil bath, and the reaction mixture was magnetically stirred. Aliquotes were taken at selected reaction times. The products were separated and analyzed by gas chromatography in a capillary column (5% methylphenylsilicone, 25-m length) and an FID detector. Identification of the different products was done by GC-MS and available reference standards. Finally, the unreacted H_2O_2 was measured by standard iodometric titration.

Table II. Binding Energy (eV) of the Ti ($2p_{3/2}$) Peak

	sample						
	1	7	10	11	Euro TS-1	ramsayite	benitoite
as-made	459.5	459.6					
calcined	459.0	459.8	459.8	459.5	460.0	459.8	460.2

Results and Discussion

Synthesis. Synthesis of zeolite β is usually carried out in the presence of Na^+ and K^+ cations. However, as we have recently reported,[10] during the synthesis of Ti-β the presence of alkali metal cations in the initial mixture has to be avoided, as they promote the formation of poorly crystalline precipitate. The solids have a high Ti content and a TiO_2/M_2O (M = Na^+ and/or K^+) molar ratio close to 1,[10] suggesting that Ti resides mainly in an amorphous titanosilicate (or titanoaluminosilicate) phase. Sample 1 in Table I was prepared in the presence of alkali cations. By contrast, in the absence of alkali cations, highly crystalline solids with X-ray diffraction patterns corresponding to the zeolite β framework are obtained.

XPS. XPS measurements were done on the as-made and calcined Ti-β samples, synthesized with and without alkali cations. Three different reference materials were also studied: Euro TS-1 (TS-1), (calcined) and two natural titanosilicates, ramsayite and benitoite. The binding energies for Ti ($2p_{3/2}$) are listed in Table II. The binding energies of the as-synthesized materials are in the range 459.5–460.0 eV, that is well above the typical value of 458.4 eV for anatase, which allows us to rule out the presence of TiO_2 even in the samples synthesized in presence of alkali cations. However, after calcination, the Ti ($2p_{3/2}$) binding energy of sample 1, synthesized in the presence of alkali metal cations, shifts to 459.0 eV, which is close to that of anatase, whereas the binding energy of this photoelectronic transition is still above 459.5 eV for the calcined samples crystallized in the absence of alkali metal cations.

The binding energy of Euro TS-1 is 460.0 eV, slightly lower than that reported for TS-1 (460.2 eV) by Carati et al.[17] and close to the value of 459.8 eV reported in ref 18 for TS-2. The latter Ti peak was attributed to tetrahedral Ti,[18] following the assignment given by Mukhopadhyay et al.[19] for Ti in TiO_2–SiO_2 glasses. The Ti ($2p_{3/2}$) peak at high binding energy detected in TS-1 was attributed to highly dispersed Ti atoms.[17] However, octahedral Ti coordination in calcined hydrated TS-1 has been reported.[20]

In an attempt to clarify the assignment of the Ti ($2p_{3/2}$) peak in Ti-containing zeolites, we have studied two natural titanosilicates with different structures, benitoite and ramsayite. In both minerals, titanium atoms occupy octahedral sites, a very distorted one in ramsayite and a symmetric one in benitoite. In the latter case, the TiO_6 units are isolated in a silica matrix.[21] Quite different and more complicated is the ramsayite structure. In this mineral there are planes built of SiO_3 chains connected by Ti ions. Thus, strings of TiO_6 octahedra, as in brookite, connect the SiO_3 chains, octahedra, and tetrahedra having corners in common.[22] The Ti ($2p_{3/2}$) peak appears in ramsayite and benitoite at 459.8 and 460.2 eV, respectively (Table II). Thus, it seems to us that the appearance of this peak at ca. 459.5 eV for our material does not

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necessarily mean that the sites are tetrahedral. However, the peak is clearly shifted to higher binding energy in benitoite and ramsayite compared to that from anatase, even if the Ti atoms are in octahedral coordination in all three compounds. Thus, the Ti ($2p_{3/2}$) peak shifts to higher binding energy when Ti atoms reside in a silicon-rich environment, i.e. having a high silicon population in the second coordination shell. Indeed, the binding energy is 0.4 eV higher in benitoite, possibly because there are no titanium atoms in the second coordination sphere of Ti.

Considering the above discussion and the binding energy values given in Table II, it can be concluded that Ti atoms in the as-made samples are present in a silicon-rich environment, even in the presence of alkali cations in the synthesis mixtures. However, the samples obtained from alkali-rich gels give, after calcination, a Ti ($2p_{3/2}$) peak which is close to that of anatase, whereas this peak from the samples obtained in the absence of alkali metals hardly changes upon material calcination and remains above 459.0 eV in all cases.

The XPS results, together with those from IR and XRD given in refs 9 and 10, suggest that Ti atoms in the samples synthesized in the presence of alkali metal cations are located in amorphous titanosilicate and are unstable when calcined. By contrast the Ti atoms in the alkali-free samples keep their silicon-rich second coordination shell even after calcination, owing to the stabilizing effect of the framework on the Ti lattice sites.

However, an unambiguous answer on the coordination of Ti located in the zeolite framework cannot be obtained from XPS measurements.

UV–Visible Diffuse Reflectance. Diffuse reflectance spectra in the UV–visible region (DR-UV) of calcined samples of zeolite β with different titanium contents are given in Figure 1.

In the spectra of the samples with the lowest Ti content, obtained in the absence of alkali metal cations, a strong peak at ca. 225 ± 5 nm can be observed. As the Ti content increases, a second peak appears at 205 ± 3 nm. Sample **5** gives a peak at ca. 212 nm and a very weak peak at ca. 270 nm. The latter is strongly enhanced, whereas that at the lower wavenumber decreases, if the zeolite crystallizes in the presence of alkali cations (spectrum 1 in Figure 1). However, no band at ~330 nm, corresponding to anatase, is detected. We suggest that the broad band at ~270 nm, also observed in the spectrum of TS-1,[23] comes from partially polymerized hexacoordinated Ti species, which contain Ti–O–Ti bonds and belong to a silicon-rich amorphous phase.[23]

A band at ca. 225 nm in the DR-UV spectrum of calcined hydrated TS-1 has been assigned to the ligand-to-metal charge transfer (CT) involving isolated titanium atoms in octahedral coordination.[24] Dehydration of this sample shifts the band to ca. 204 ± 4 nm, characteristic for a CT transition involving tetracoordinated Ti(IV) in the [TiO_4] or [TiO_3OH] structure.[25]

According to this assignment, the peak at ca. 225 nm from Ti-containing zeolite β may come from the isolated hexacoordinated Ti(IV) atoms. The Ti(IV) atoms in a lower coordination state, probably tetracoordinated, should then be responsible for the peak at ca. 205 nm. Indeed, for sample **5** the main peak appears with a wavenumber between those attributed to four- and sixfold Ti atoms in the framework. We speculate that pentacoordinated Ti atoms are preferred in this calcined hydrated sample, although minor amounts of tetrahedral and octahedral Ti sites may still be present (cf. X-ray absorption results).

X-ray Absorption. Two samples synthesized from initial mixtures with and without alkali cations were characterized (samples **1** and **5**, see Table I).

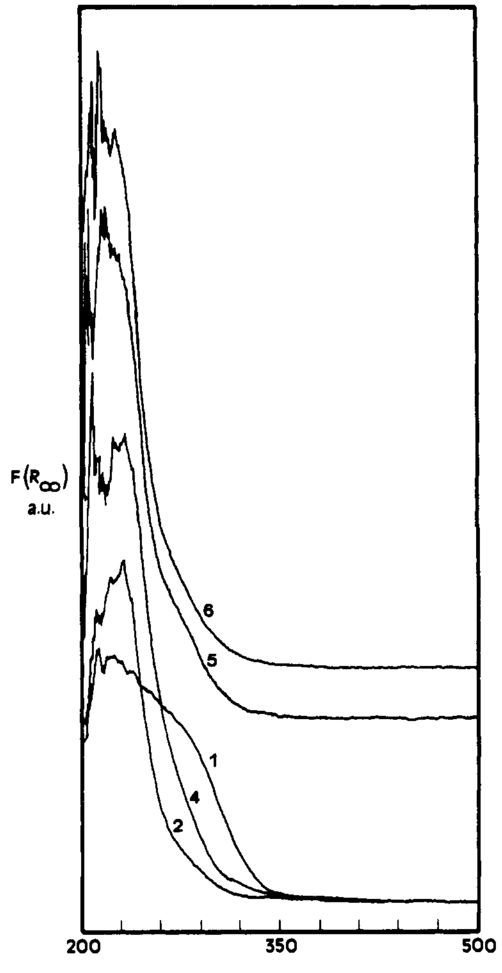

Figure 1. Diffuse reflectance UV–visible spectra of different Ti-containing β samples. Numbers in figure correspond to sample numbers in Table I.

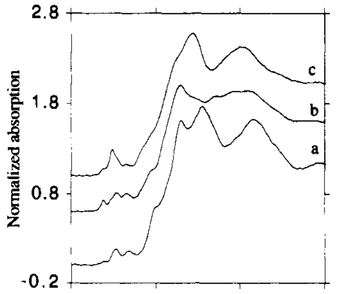

Figure 2. Ti *K*-edge XANES spectra of (a) TiO_2 rutile, (b) TiO_2 anatase, and (c) ramsayite.

XANES. The edge region in the absorption spectra provides much information on the environment geometry and the electronic structure of the absorbing atom. In particular, a comparison of the XANES spectra with those of model compounds allows one to determine the site symmetry of the absorber in the sample.

Figure 2 shows the XANES spectra of three different compounds used in this present work as standards: rutile and anatase oxides (TiO_2) and the natural titanosilicate ramsayite ($Na_2Ti_2Si_2O_2$). The three spectra have three pre-edge features, hereafter referred to as A_1, A_2, and A_3, characteristic of titanium ions in an octahedral environment.[26] Although the interpretation of the A_1 peak is still controversial, the A_2 and A_3 peaks are

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Table III. Pre-Edge Peak Parameters for Titanium Reference Compounds

compound	titanium site symmetry	peak position[a] (eV) $A_1/A_2/A_3$	intensity[b]	half-height width (eV)	ref
anatase	distorted octahedral	2.5/5.5/8.0	0.13/0.21/0.21		this work
rutile	distorted octahedral	2.7/5.5/8.7	0.04/0.18/0.16		this work
ramsayite	very distorted octahedral	2.8/4.8/8.5	0.08/0.29/0.13		this work
titanyl phthalocyanine	square pyramidal	4.5	0.79	1.9	32
fresnoite	square pyramidal	4.0	0.60		29
Ba_2TiO_4	distorted tetrahedral	3.5	0.84	1.5	32

[a] Relative to the first inflection point for Ti metal. [b] Relative to the beginning of the EXAFS oscillations.

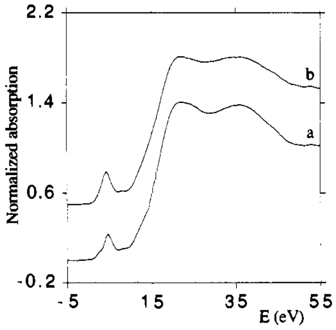

Figure 3. Ti *K*-edge XANES spectra of the Ti-β sample prepared in the presence of alkali cations: (a) as-synthesized and (b) calcined.

attributed to the 1s → t_{2g} and e_g electronic transitions, respectively.[26,27] The energies and intensities of the pre-edge peaks for the reference structures are summarized in Table III. It has been previously shown[28,29] that a substantial distortion of the octahedral Ti site results in an increase of the A_2 peak intensity. In ramsayite, Ti resides in a very distorted octahedral site with six different Ti–O distances ranging from 1.81 to 2.91 Å.[22] In titanium oxides only two different Ti–O bonds, 1.93 and 1.98 Å long in anatase[30] and 1.95 and 1.98 Å long in rutile,[31] are present, so the intensity of the A_2 prepeak in these oxides is lower than that in ramsayite. Another difference between titanium oxides and ramsayite is observed for the position of the A_2 peak (XANES spectra in Figure 2). Our results resemble those of Waychunas,[28] who observed a shift of the A_2 peak in silicates by about 0.6 eV toward lower energy when compared to the case of oxides (Table III).

Literature XANES data on titanium atoms in tetrahedral or square pyramidal environments are also included in Table III. The lack of inversion symmetry in the tetrahedral environment results in a single intense prepeak, shifted about 2 eV toward lower energy with respect to the A_2 peak of octahedral sites in oxides. This peak is assigned to the allowed 1s → t_2 transition for tetrahedral symmetry.[27] For pentacoordinated titanium, a single prepeak is also observed. This appears at ca. 4.5 eV in titanyl phthalocyanine and is also shifted by about 0.5 eV toward lower energy in fresnoite silicate (Table III).

Figure 3 shows the Ti *K*-edge spectra of the catalyst, as-prepared and calcined, synthesized in the presence of alkali metal cations. The as-prepared sample gives three prepeaks typical of octahedral Ti sites (Table IV). We note that the energy of the A_2 peak is quite similar to that of ramsayite, so Ti atoms are probably in a silicate surrounding. This is in agreement with the formation of amorphous titanosilicate, and it is also consistent with the assignment of the Ti ($2p_{3/2}$) peak at ca. 459.5 eV in the XPS spectra to Ti atoms having Si atoms in the second coordination shell. We believe that this distorted octahedral arrangement is predominant but a minor amount of Ti in lower coordination states can still be present. After calcination, the intensity of the peak increases, which makes the detection of the A_1 peak difficult. We suppose that this intensity increase is due to the occurrence of some Ti atoms in a lower coordination symmetry (tetrahedral and/or square pyramidal), exerted by the loss of some labile ligands. However, the possibility of an even higher distortion in the titanium environment produced by calcination cannot be ruled out. Considering also the results obtained from DR-UV, we conclude that in the calcined state there is a mixture of Ti sites with different environments. Some of the Ti atoms are located in octahedral positions in an amorphous titanosilicate phase, whereas the others occupy framework sites having coordination numbers lower than 6.

Figure 4 and Table IV show the XANES spectra and pre-edge peak parameters, respectively, corresponding to the catalyst prepared from the alkali-free reaction mixture. The three spectra show only one pre-edge feature with increasing intensity for the as-synthesized, calcined, and calcined dehydrated samples.

The most remarkable feature of these data is the position of the prepeak, which is very close to that of Ti in a tetrahedral environment or to pentacoordinated Ti bonded to silicate units (see Table III). The lower intensity and the larger line width observed for the catalyst in the as-prepared samples can originate from a mixture of various symmetry sites.[18,20,29]

The position of the prepeak for the as-prepared sample indicates that Ti exists in tetracoordinated species. However, thermogravimetric analysis shows that the OH^-/Ti ratio is close to 1,[10] and EXAFS gives a coordination number close to 5.5 (vide infra). These observations, together with the fact that pentacoordinated Ti in silicates gives a prepeak at ca. 4.0 eV,[29] suggest that in the as-prepared sample there must be an appreciable amount of pentacoordinated Ti. The lower intensity of the prepeak with respect to that of fresnoite could be due to the coexistence of some octahedral Ti. Indeed, the assignment of XANES peaks to pentacoordinated Ti is consistent with the assignment of the most intense band in the DR-UV spectrum to the charge transfer in such pentacoordinated species. Nevertheless, the presence of minor amounts of tetrahedral titanium cannot be ruled out.

A sharper and much more intense XANES prepeak is obtained for the calcined dehydrated catalyst, which indicates a change from octahedral to lower Ti coordination. In fact, EXAFS results (vide infra) suggest a tetrahedral environment for Ti, possibly created by elimination of some of its ligands during calcination. Finally, an intermediate situation could be suggested for the calcined hydrated catalyst (see Figure 4b and Table IV), since the initial Ti environment is not reconstituted and most of the Ti

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Table IV. Pre-Edge Peak Parameters for Ti-β Catalysts

sample		peak position[a] (eV) $A_1/A_2/A_3$	intensity[b]	half height width (eV)
alkali-containing Ti-β	as-synthesized	2.3/4.5/8.0	0.09/0.23/0.10	
	calcined	—/4.5/8.0	—/0.29/0.12	
alkali-free Ti-β	as-synthesized	3.7	0.32	1.9
	calcined	3.7	0.40	1.5
	calcined dehydrated	3.8	0.58	1.5

[a] Relative to the first infection point for titanium metal. [b] Relative to the beginning of the EXAFS oscillations.

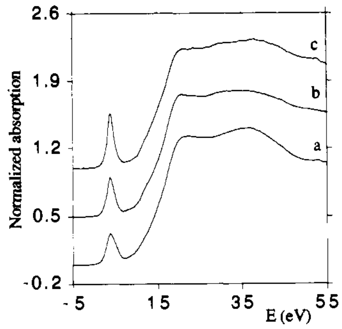

Figure 4. Ti K-edge XANES spectra of the Ti-β sample prepared in the absence of alkali cations: (a) as-synthesized, (b) calcined, and (c) calcined dehydrated.

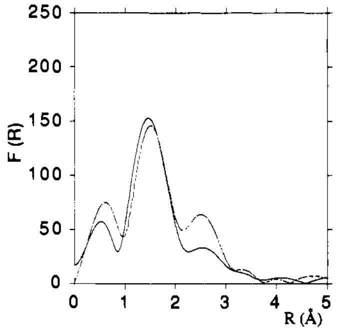

Figure 5. Fourier transform magnitude of the K^3-weighted EXAFS signal of the Ti-β sample prepared in the presence of alkali cations in the as-synthesized (dashed line) and calcined (solid line) states.

atoms remain in a low coordination state. The lower intensity of the prepeak in Figure 4c compared with that of tetrahedral Ti in Ba_2TiO_4 can be explained either by differences in the site geometry[33] or, more probably, by the coexistence of various environments, though to a lesser extent than in the as-prepared sample.

It is interesting to compare our results for zeolite β with those reported for silicalite type materials, i.e. TS-1 and TS-2. Behrens et al.[29] found that in as-prepared TS-1 the octahedral symmetry is dominant, although tetrahedral and square pyramidal environments were also detected. They did not observe any significant influence of calcination on the pre-edge features. A similar XANES spectrum was reported by Lopez et al.,[20] who observed that a dehydration of calcined TS-1 was necessary to obtain tetrahedral Ti as the major species (one prepeak at 3.8 eV with a relative intensity of 0.50). A different behavior was reported[20] for the reference TS-1 sample synthesized in the presence of F^- ions, since calcination produced an appreciable amount of tetrahedral Ti, as was deduced from the intense prepeak (0.49) shifted toward lower energy (4.1 eV). Recently, Trong On et al.[18] have studied by XANES the effect of loading on the symmetry of the Ti environment in a series of calcined TS-2 catalysts. For the samples with a low Ti content only one intense (0.40–0.50) prepeak at ca. 3.9 eV was found and assigned to a mixture of tetrahedral and square pyramidal environments, a coordination state similar to that proposed for calcined Ti-β in our work. To summarize, while dehydration of calcined TS-1 is necessary to generate an appreciable amount of low-coordinated Ti, such species are abundant in as-synthesized Ti-β. An intermediate behavior is observed for TS-2 and for TS-1 synthesized in the presence of F^- ions. In the latter sample there are some F^- ions in the close vicinity of Ti atoms,[20] and these can interact with Ti lattice sites, as it has also been observed for OH^- ions in zeolite Ti-β. At present it is unclear to us why the interaction between such electron-donor species and Ti atoms leads in crude crystals to low-coordinated Ti atoms after calcination.

EXAFS. Figure 5 shows the modulus of the Fourier transform of the EXAFS signals from Ti-β crystallized in the presence of alkali metal cations, the samples being as-prepared and calcined. Both spectra show a first peak at ca. 1.5 Å (without phase correction) due to oxygen neighbors.

The best fit obtained for the first coordination shell of Ti yields the results collected in Table V. Both the coordination number and the mean Ti–O distance (1.95 Å) calculated for the as-prepared catalyst suggest that most of the Ti atoms are octahedrally coordinated, in good agreement with the XANES results. The slight decrease in the coordination number observed upon calcination must be related to the formation of some low-coordinated Ti atoms. The high Debye–Waller factor values relative to the reference, obtained in the simulation of the first coordination shell using spectra given in Figure 5, must be due to the occurrence of different sites, since some Ti atoms occupy framework positions in the zeolite β and others are forming amorphous titanosilicates as shown by DR-UV. This disorder renders the fittings difficult. We tried to improve the fitting by simulation of the experimental data using two different Ti–O distances, without any success.

The radial distribution functions for the alkali-free Ti-β are shown in Figure 6. The as-synthesized catalyst gives only one peak at about 1.4 Å (without phase correction) due to oxygen scatterers in the first coordination sphere of titanium. After calcination and dehydration, a second peak grows at distance of 2.8 Å. This peak is also observed, although with lower intensity, in the spectrum of the calcined material, and it is not shown in Figure 6 for the sake of clarity. The lack of the second coordination shell in the as-synthesized material could be due to a large distortion of the Ti environment, which is possibly removed by calcination.

Comparison of Figures 5 and 6 shows that the intensity of the first peak is higher in the latter case. The best fitting parameters from the analysis of the first coordination shell of the alkali-free catalysts are collected in Table V. The comparison of the results obtained for samples prepared in the presence and absence of alkali cations clearly indicates that the lower intensity of the first peak in the Fourier transformed spectra of the former is caused by a higher disorder (high Debye–Waller factor) in the environment; thus, a lower coordination reason can be ruled out.

For the alkali-free as-prepared catalyst, the mean Ti–O distance is shorter than that in the sample containing alkali cations, and the mean coordination number is ca. 5.5. This is consistent with the XANES conclusions on a coexistence of some penta- and hexacoordinated Ti. Since the thermogravimetric measurements indicate a OH^-/Ti ratio of ca. 1,[10] we suppose that the framework Ti atom must be coordinated to four oxygens (vide infra) and one

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[33] Emili, L.; Incoccia, L.; Fagherazzi, G.; Guglielmi, M.; *J. Non-Cryst. Solids* **1985**, *74*, 129.

Table V. EXAFS Simulation Parameters Obtained in the Fitting of the First Coordination Shell of Ti-β Zeolites Corresponding to Oxygen Neighbors

sample		N (±0.5)	R (Å)	$\Delta\sigma$ (Å)	$\Delta E°$ (eV)	fit value
alkali-containing Ti-β	as-synthesized	5.9	1.95 ± 0.02	0.109	2.7	1.7×10^{-2}
	calcined	5.5	1.94 ± 0.02	0.100	3.3	1.3×10^{-2}
alkali-free Ti-β	as-synthesized	5.5	1.92 ± 0.02	0.052	2.8	2×10^{-3}
	calcined dehydrated	4.2	1.87 ± 0.02	0.040	5.3	5×10^{-3}
	calcined	3.6	1.86 ± 0.02	0.000	4.4	6×10^{-3}
		3.9	1.87 ± 0.02	0.020	5.2	
		1.0	2.27 ± 0.05	0.020	5.2	4×10^{-3}
		3.0	1.85 ± 0.02	0.020	4.7	
		0.9	1.93 ± 0.05	0.020	4.7	7×10^{-3}

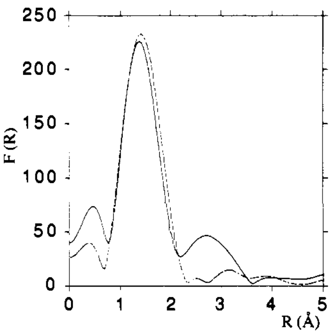

Figure 6. Fourier transform magnitude of the K^3-weighted EXAFS signal of the Ti-β sample prepared in the absence of alkali cations: as synthesized (dashed line) and calcined dehydrated (solid line).

OH⁻ group and that occasionally an extra water ligand makes it hexacoordinated. Calcination followed by dehydration reduces the Ti coordination down to four oxygen atoms with a concomitant decrease of 0.05 Å in the Ti–O mean distance. A similar (within the experimental error) Ti–O bond length has been previously reported for tetrahedral Ti in glasses[34] and in TS-2[18] on the basis of EXAFS measurements. A slightly lower Ti–O distance (1.83 Å) has been calculated from EXAFS[20] for tetracoordinated Ti in TS-1. The above arguments point to tetrahedral Ti as the most abundant species in the dehydrated catalyst.

For the calcined material a good fit was obtained for 3.6 oxygen atoms at 1.86 Å, suggesting that Ti does not change its coordination state after rehydration. Nevertheless, in order to explain the decrease of the prepeak in the XANES spectrum, we decided to explore other possible solutions involving changes in site symmetry and coordination and we also used two different Ti–O distances. The best sets of simulation parameters are presented in Table V. The first solution assumes a pentacoordinated Ti site to exist with four oxygen atoms at a mean distance of 1.87 Å and a fifth oxygen atom located much further away (2.27 Å), the latter probably belonging to a water molecule. The second solution places Ti inside a tetrahedron with three equivalent Ti–O distances, probably due to oxygens shared with SiO_4 (or AlO_4) units, and with a longer distance (1.93 Å), probably from an OH⁻ group. X-ray absorption does not allow us to choose between those solutions, and therefore we cannot assess whether the sample contains penta- or tetracoordinated Ti. Maybe there is just a mixture of both species, as indicated by the already discussed DR-UV results.

In order to get further information on the surrounding of Ti in alkali-free β-Ti, the second peak in the spectrum of the calcined dehydrated catalyst has been analyzed. The peak is shifted to longer distances with respect to the case of anatase, so the second coordination sphere in the material is not due to the presence of extraframework anatase particles. The fittings of the experimental filtered data using longer Ti–Ti distances were not satisfactory. Then, we tried to simulate the signal using the Mckale[16] functions for the Ti–Si pair (Figure 7, Table VI). It is interesting to stress here that, due to the fact that Si and Al have very close Z numbers, their backscattering amplitude functions are quite similar and it is not possible to distinguish between them by EXAFS. Thus, although throughout the discussion we will refer to silicon tetrahedra, as they are more abundant, we cannot forget that AlO_4 tetrahedra can also be present in the second coordination shell of titanium. A good fitting is obtained for four silicon atoms in the second shell of Ti at a distance of about 3.23 Å, which implies the existence of isolated TiO_4 units. The fitting was slightly improved by substitution of one Si by one Ti at 3.09 Å (Figure 8, Table 6), which would indicate the presence of pairs of TiO_4 tetrahedra. Since it has not been possible to find an appropriate reference for Ti–Si and Ti–Ti, this analysis is not quantitative and we use it only for an assessment of the possible solutions. Thus, although EXAFS results indicate that the second coordination shell of titanium contains mainly silicon backscatterers, we cannot completely rule out the existence of pairs of TiO_4 tetrahedra. The Si–O bond length of tetrahedral silicon is around 1.62 Å, and the Si–Si distances in silicates and zeolites are approximately 3.00 Å. In natural silicates, benitoite and ramsayite, in which titanium atoms are octahedrally coordinated and sharing corners with silicon tetrahedra, the Ti–Si distance is around 3.30 Å. It follows that in our sample the Ti–Si distances correspond to tetrahedral TiO_4 units sharing corners with SiO_4 tetrahedra, thus confirming the incorporation of Ti into the structural positions of the zeolite β network. In fact, assuming

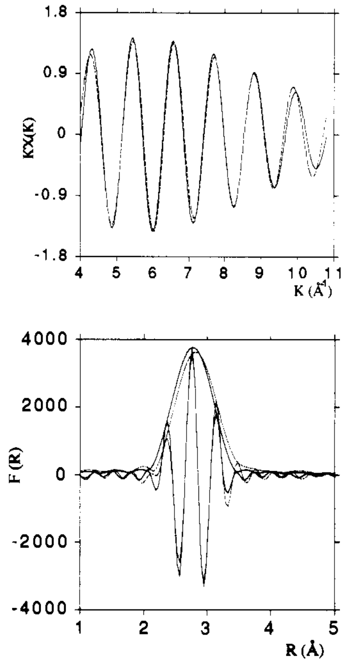

Figure 7. Comparison between the calculated (solid line) and experimental (dashed line) data corresponding to the second coordination shell around Ti in the Ti-β sample prepared in the absence of alkali cations, with Si as backscattering atoms. The theoretical Mckale functions were used to simulate the signal: (top) K-space and (bottom) modulus and imaginary part of the Fourier transform.

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(34) Dumas, T.; Petiau, J. *J. Non-Cryst. Solids* **1986**, *81*, 201.

Table VI. EXAFS Simulation Parameters Obtained in the Fitting of the Second Coordination Shell of Ti-β Zeolite[a]

sample	backscattering atom	N (±0.5)	R (Å) (±0.05)	σ (Å)	Γ (Å^{-2})	ΔE (eV)	fit value
calcined dehydrated	Si	4[b]	3.23	0.055	1.48	2.5	3.5×10^{-2}
alkali-free	Si	2.8	3.25	0.070	1.51	4.8	
Ti-β	Ti	1.2	3.09	0.070	1.51	4.8	1.2×10^{-2}

[a] Theoretical Mckale phase and backscattering functions[16] were used in the calculation. [b] Value fixed in the fitting.

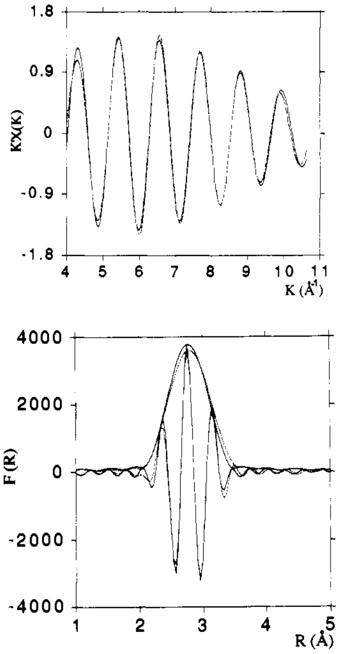


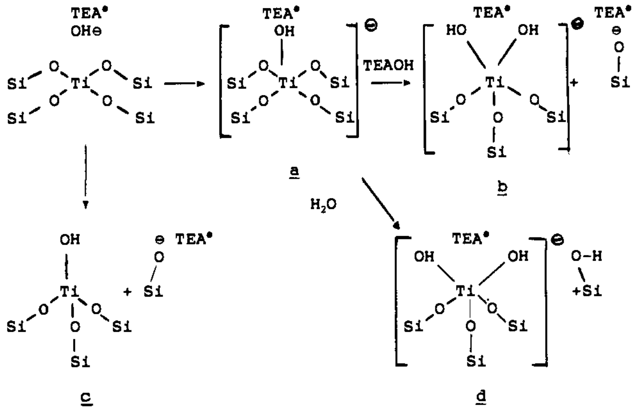
Figure 8. Comparison between the calculated (solid line) and experimental (dashed line) data corresponding to the second coordination shell around Ti in the Ti-β sample prepared in the absence of alkali cations, with Si and Ti as backscattering atoms (see Table VI). The theoretical Mckale functions were used to simulate the signal: (top) K-space and (bottom) modulus and imaginary part of the Fourier transform.

a Si–O distance of 1.62 Å, i.e. the most common in zeolites, and the Ti–O and Ti–Si distance obtained by EXAFS (1.87 and 3.23 Å, respectively), we have estimated the Ti–O–Si angle to be approximately 138°, which is slightly lower than that reported for (Al, Si) zeolite β.[35]

The results of our work are in contrast with those found in the literature for silicalite materials. A shorter Ti–Si distance (2.8 Å) was reported by Schultz et al.[36] in the EXAFS fitting of the second coordination shell for TS-1, indicating a large distortion of the framework by substitution of Ti for Si. Very different results have been recently published by Trong On et al.[18] for TS-2. They reported very short Ti–Si (2.2 Å) and Ti–Ti (2.6 Å) distances, which are not consistent with isomorphous substitution of titanium by silicon in the zeolite framework. The results were interpreted in terms of edge-sharing tetrahedra with the presence of both monomeric and dimeric titanium species.

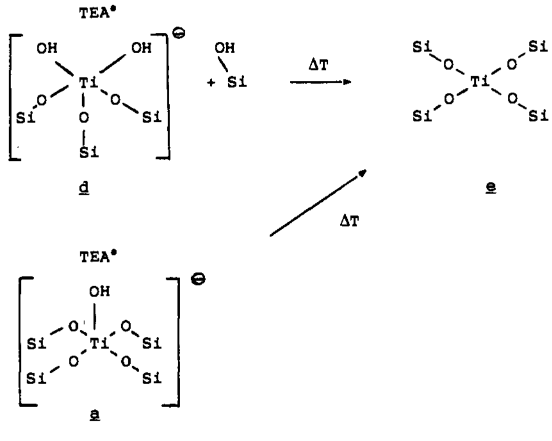
Coordination Model of Ti in Zeolite β. A model that explains the coordination state of titanium atoms in the crystal lattice of zeolite β can be constructed on the basis of data discussed above. In the as-synthesized sample, five-fold coordination prevails, although also some six-coordinated Ti atoms must be present. TEAOH species interact strongly with titanium, and IR absorption occurs in the 950–990-cm^{-1} region. In the hydrated calcined sample, penta- and probably also tetracoordinated titanium exists. These samples show an intense 960-cm^{-1} IR band, which has been assigned to a Si–O stretching vibration within the Si–OH group.[11] Dehydration of calcined samples leads to Ti in fourfold coordination. The second coordination sphere of Ti is formed by silicon atoms, although the presence of single Ti atoms in this shell cannot be completely excluded.

Accordingly we propose the following scheme for the as-made material:

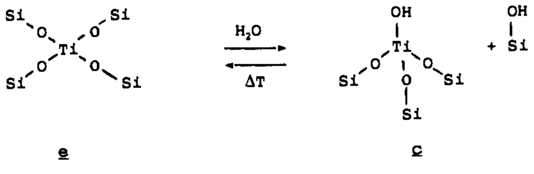


Coordination of extra H_2O molecules increases the Ti coordination to six (species **d** and **b**) or five (species **c**), in agreement with the XANES-EXAFS results. In the scheme the (Ti–OH)$^{3+}$ group is supposed to play a role equivalent to a trivalent cation, like Al^{3+}, according to the competion observed between Ti and Al during the crystallization of zeolite.

Species **d**, **b**, and **c** should be transformed under heating into the four-coordinated Ti species (species **e**).



Considering the calcined hydrated samples, addition of a water molecule to species **e** would hydrolyze one Si–O–Ti bond,[37] keeping the four-fold coordination of Ti intact (structure **c**).



Further addition of another water molecule to species **c** without bond dissociation would generate fivefold-coordinated titanium.

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(35) Newsam, J. M.; Treacy, M. M. J.; Koetsier, W. T.; Gruyter, C. B. *Proc. R. Soc. London, A* **1988**, *420*, 375.

(36) Schultz, E.; Ferrini, C.; Prins, R. *Catal. Lett.* **1992**, *14*, 221.

(37) Bellussi, G.; Carati, A.; Clerici, M. G.; Maddinelli, G.; Millini, R. *J. Catal.* **1992**, *133*, 220.

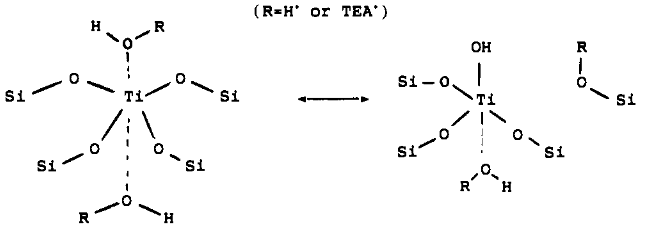
Table VII. Catalytic Activity of Ti-β (Sample 6) and Ti-Silicalite (TS-1) for Cyclohexane and Cyclohexanol Oxidation

catalyst	substrate	conversion (H_2O_2) (mol %)	H_2O_2 yield[c]	reaction time (h)
TS-1	cyclohexanol[a]	39	40	3.5
Ti-β	cyclohexanol[a]	85	58	3.5
TS-1	cyclohexene[b]	<1		3.5
Ti-β	cyclohexane[b]	80	83	3.5
TS-1	1-hexene[b]	98	80	3.0
Ti-β	1-hexene[b]	80	80	3.0

[a] Reaction conditions: 353 K, 33 mmol cyclohexanol, 0.827 g of H_2O_2 (35 wt %), 23.57 g of *tert*-butyl as solvent, and 0.200 g of catalyst. [b] Reaction conditions: 298 K, 33 mmol olefin, 0.264 g of H_2O_2 (35 wt %), 23.57 g, methanol as solvent, and 0.200 g of catalyst. [c] H_2O_2 yield = moles of substrate oxidized/moles of H_2O_2 converted.

Both hydrated and dehydrated species **c** are consistent with the EXAFS results (Table V).

The structures **c** and **e** are coupled by water exchange, and this model can be extended to the interaction of TEAOH with the Ti atoms. In general, the process can be represented as follows:



Catalytic Results. Even though the different physicochemical technique can support the location of Ti in the zeolite framework, the real fingerprint for this type of materials is their catalytic activity for oxidation reactions. It has been extensively shown[1,3] that only those materials in which Ti is in framework positions are active for carrying out catalytic oxidation with H_2O_2. On the contrary, those titanium zeolites in which Ti is not in the framework are inactive as oxidation catalysts, regardless the presence of the 960-cm^{-1} IR band.

Results from Table VII show that the Ti-β zeolite is active for olefin and alcohol oxidation. When the activity of the Ti-β is compared with that of the Euro TS-1, it can be seen that the Euro TS-1 is more active than Ti-β for the less bulky 1-hexene but sensibly less active for cyclohexene and cyclohexanol, which present geometrical constraints for diffusion in the smaller pores of the TS-1 sample. As could be expected, sample 1, which was obtained in the presence of alkali cations and which does not have Ti in zeolite framework positions, was completely inactive for carrying out the oxidation reactions.

Conclusions

Various characterization techniques used in our work have brought the following conclusions:

Ti-β zeolites synthesized in the presence of alkali metal cations contain a titanosilicate phase, where Ti is octahedrally coordinated, and a Ti-β phase, where Ti is from four to six coordinated depending on the posttreatment conditions.

From alkali-free solution highly crystalline Ti-β zeolite is formed. In the as-synthesized sample Ti exists in both hexa- and pentacoordinated forms, the latter being predominant. Such Ti atoms are isolated and have the closest Ti neighbor separated by Ti–O–Si–O–Ti bonds, but a minor population of Ti–O–Ti pairs cannot be completely ruled out.

The pentacoordinated Ti atom is bound to four O–Si groups and one OH$^-$ group, the negative charge being compensated by TEA$^+$ (structure **a**). If one molecule of H_2O or TEAOH reacts with the species **a**, then the pentacoordinated species **d** and **b** are formed.

After calcination and dehydration the coordination number of Ti decreases from 5 to 4 (species **e**), and in this coordination state Ti is linked to four O–Si groups. When the calcined zeolite is rehydrated, a Ti–O–Si bond becomes hydrolyzed, giving the tetrahedral species **c** and a silanol group.

After rehydration, the initially formed tetrahedrally coordinated Ti species **c** can be further hydrated leading to pentacoordinated Ti.

Our results for zeolite Ti-β can be compared with those on TS-1 and TS-2 from the literature.[18,20,29,36] It appears that in the calcined hydrated samples a similar first coordination shell of Ti occurs in β and TS-2, and even in TS-1 when it is synthesized in the presence of F$^-$ anions. However the coordination is different for TS-1, which shows a six coordination for Ti.

Finally the Ti-β samples synthesized in the absence of alkaline cations are active for carrying out the oxidation of olefins, cycloolefins, and alcohols.

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