Catalysis Letters 34 (1995) 101–113

X-ray absorption spectroscopy of Ti-containing molecular sieves ETS-10, aluminum-free Ti-β, and TS-1

R.J. Davis[1], Z. Liu, J.E. Tabora and W.S. Wieland

Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22903-2442, USA

Received 31 March 1995; accepted 26 May 1995

We report here the first structural characterization by Ti K-edge EXAFS and XANES of ETS-10 and aluminum-free Ti-β molecular sieves. A TS-1 sample was also studied for comparison. The near-edge spectrum of TS-1 revealed an intense pre-edge feature characteristic of Ti atoms in tetrahedral coordination. However, the pre-edge peak for ETS-10 was quite small and shifted in energy, which is consistent with the known octahedral structure surrounding Ti atoms in the material. Analysis of the EXAFS for ETS-10 revealed an average Ti–O interatomic distance of 2.00 ± 0.01 Å which is longer than the Ti–O distance (1.95 Å) in anatase TiO_2. For Ti-β, an intense pre-edge peak is present in the near-edge spectrum and the intensity, energy and width of this peak are the same as for TS-1. In addition, the average Ti–O interatomic distance in Ti-β and TS-1 was 1.80 ± 0.01 Å, which is significantly shorter than the distance measured in ETS-10. The EXAFS and XANES results indicate that the Ti sites in aluminum-free Ti-β are structurally identical to the tetrahedral sites in TS-1. This conclusion is supported by the similarity of the UV absorption thresholds for the two samples. X-ray absorption spectra were also recorded with methanol or 2-propanol adsorbed on the Ti-β and TS-1 molecular sieves. Alcohol adsorption decreased the intensity and broadened the Ti pre-edge peak for both samples, demonstrating a local chemical interaction with the Ti sites. Methanol adsorption lengthened the average Ti–O bond to 1.83 ± 0.01 Å. The similarity of the X-ray absorption spectra for aluminum-free Ti-β and TS-1 in the presence of alcohols suggests that the Ti sites in the two frameworks are chemically indistinguishable for vapor-phase adsorption of alcohols at low concentrations.

Keywords: ETS-10; TS-1; Ti-β; EXAFS; XANES; X-ray; UV; methanol; 2-propanol

1. Introduction

Titanosilicalite, TS-1, is a well-known catalyst for the selective oxidation of a wide variety of hydrocarbons with aqueous hydrogen peroxide [1], but the relatively small pore size of TS-1 (∼ 6 Å) prevents this important material from catalyzing reactions of large molecules. Therefore, ongoing work focuses on discovering

---

[1] To whom correspondence should be addressed.

why TS-1 exhibits such unique catalytic activity in order to design new, large pore molecular sieve analogs. Recent structural investigations involving X-ray, UV, and IR spectroscopies conclude that Ti atoms in TS-1 substitute for Si atoms in normal tetrahedral framework sites [2], and that the addition of small molecules, such as water and ammonia, to TS-1 greatly perturbs the regular tetrahedral oxide structure surrounding Ti atoms in the framework [3]. The ease with which Ti can change its coordination environment in the presence of reactive molecules most likely accounts for its chemical reactivity. An exceptional property of TS-1 is that it catalyzes reactions in the presence of water, a known inhibitor of transition metal oxide catalysts. One theory is that the highly hydrophobic micropores of TS-1 effectively screen out water from the active Ti sites during catalysis [4]. Another interesting feature of selective oxidation catalysis by TS-1 is the effect of co-solvent on the reaction rate. For example, the rate of propene epoxidation by aqueous hydrogen peroxide in the presence of alcohol co-solvent follows the order: methanol > ethanol > *t*-butanol [5]. A definitive explanation for the effect of alcohols on catalysis by TS-1 has not yet been presented but most likely involves an induction effect from the alkyl group on the alcohol and a steric effect for the larger alcohols in the pores of TS-1 [5].

Recently, Ti-containing zeolite β was synthesized and shown to be active for selective oxidation of olefins and alkanes with aqueous hydrogen peroxide using an alcohol co-solvent [6]. Since the β sample also contained framework aluminum atoms, it will be referred to as Ti-Al/β in this paper. In that work, molecules of varying dimensions were oxidized in the presence of Ti-Al/β and TS-1. The catalytic activity of Ti-Al/β was superior to that of TS-1 for oxidation of large molecules, presumably due to the larger pore size of zeolite β. Also, the effect of alcohol size on reaction rates over Ti-β is minimal, in contrast with the large effect observed over TS-1. Again, the wider pores of zeolite β apparently eliminate the steric restrictions on bulkier alcohols. These encouraging results suggest that large pore analogs of TS-1 can be prepared and used as selective oxidation catalysts.

Results from EXAFS and XANES studies of Ti-Al/β indicate that Ti probably substitutes in the tetrahedral sites normally occupied by Si or Al [7]. However, this conclusion is based mostly on a second-shell analysis of the EXAFS, which is known to be unreliable for these materials. Indeed, the highly reliable first-shell Ti–O distance derived from EXAFS of a dehydrated Ti-Al/β sample is reported to be 1.87 Å [7], which is much longer than the distance of 1.80 Å found in TS-1 [2]. This dehydrated Ti(Al)β probably has Ti atoms in mixed states of coordination. In addition, the previous structural studies were performed on samples that contain Al, which is detrimental to oxidation catalysis. For example, Corma et al. observed that the intrinsic activity of Ti sites in Ti-Al/β for selective oxidation of cyclohexene decreased as the Al content of the framework increased [6]. Therefore, studies of an aluminum-free Ti-β would provide a more appropriate comparison with TS-1 than earlier work on Al-containing samples.

We report here for the first time structural investigations of aluminum-free Ti-β by UV reflectance and X-ray absorption spectroscopies which are then compared to results for TS-1. Additionally, we examine the effects of methanol and 2-propanol adsorption on the X-ray absorption spectra of TS-1 and Ti-β. A sample of ETS-10, a new titanium silicate molecular sieve developed by Engelhard Corp. in which Ti is coordinated octahedrally to oxygen [8], was also studied in order to compare the effect of coordination state on local structural parameters.

2. Experimental

2.1. MATERIALS

The TS-1 used in this work was synthesized according to procedures described by Taramasso et al. [9], and the ETS-10 was a commercial sample made by Engelhard Corp. The aluminum-free Ti-β, obtained from ARCO Chemical Company, was prepared by a new synthesis method [10] that is briefly summarized below. 30 g of tetraethylorthosilicate (TEOS) were added dropwise to 50 g of 0.5 N (hydroxide basis) aqueous 4,4′-trimethylenebis(N-benzyl-N-methylpiperidinium) dihydroxide solution and stirred for 1 h. Next, a second solution containing titanium tetrabutoxide (1.74 g) in TEOS (5 g) was added to the mixture. Finally, 158 g of additional 0.5 N aqueous 4,4′-trimethylenebis(N-benzyl-N-methylpiperidinium) dihydroxide were added to the precursor solution, which was then stirred for 2 h. All hydrolysis reactions were performed under a gentle flow of nitrogen. Ethanol formed during hydrolysis was removed by sparging the solution at 333 K. This gel solution was aged overnight at room temperature (RT) and heated to 408 K for nine days in agitated, teflon-lined autoclaves. The resulting crystallized solids were filtered, washed with water, and dried at 383 K. Calcination of Ti-β for 8 h in dry air at 823 K was sufficient to completely remove the organic template. Elemental compositions were provided by Galbraith Laboratories and dinitrogen adsorption isotherms were recorded on an Omnisorp 100CX instrument.

2.2. UV REFLECTANCE SPECTROSCOPY

A Beckman DU-7 spectrophotometer equipped with a Labsphere, Inc. RSA BE-70 reflectance accessory was used to record the ultraviolet reflectance spectra of the powder samples in air. Normalized absorption spectra were derived from the reflectance data according to the Kubelka–Munk formalism [11] using a Labsphere, Inc. SRS-99-010 white reflectance standard.

2.3. X-RAY ABSORPTION SPECTROSCOPY AT THE TI K EDGE

The X-ray absorption experiments were performed on beam line X18B at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York, in the transmission mode of data collection. The storage ring operated with an electron energy of 2.5 GeV with beam currents ranging from 100 to 200 mA. Higher harmonics in the beam were rejected by detuning the Si(220) monochromator crystals to 50% of the maximum intensity. As an energy calibration standard, a 4 μm thick Ti foil (Goodfellow) was placed between the second and third ionization chambers, all of which were filled with a He/N_2 mixture to optimize sensitivity. The entrance slits were adjusted to 1 × 16 mm during data collection.

The ETS-10 powder sample was placed in a thin sample holder with Kapton windows. The thickness of the sample was adjusted to give $\Delta\mu x = 0.8$ at the Ti K edge. Since Ti is octahedrally coordinated in ETS-10, no special effort was made to exclude air from the sample. However, it is well-known that ambient humidity can affect the coordination state of TS-1 and Ti-β [3,7]. Therefore, a special cell that enables in situ treatment of catalyst samples was used for examining TS-1 and Ti-β. First, each sample was diluted in BN powder and then pressed to form a self-supporting wafer. Due to the very low contents of Ti in the catalysts, $\Delta\mu x$ was typically about 0.1 for the pellets. Next, a wafer was loaded into the cell and dehydrated in flowing He (99.99%) for 1 h at 573 K. After cooling to RT and acquiring data, a sample was exposed to a flowing methanol/helium mixture prepared by passing the He carrier gas through a methanol (Baker, HPLC grade) saturator maintained at 273 K. Spectra were recorded both during and after exposure to methanol. A sample was then heated to 573 K in flowing He to regenerate the original state of the catalyst, cooled to RT, and subsequently exposed to a 2-propanol/helium mixture prepared by passing He through a 2-propanol (Mallinckrodt, Analytical Reagent grade) saturator maintained at 273 K. Both alcohols were dried over molecular sieves before use.

The EXAFS data were processed with Macintosh versions of the University of Washington analysis programs. Anatase powder (Aldrich, 99.9%) was used as the reference material for structural information (interatomic distance, R; coordination number, N; and change in Debye–Waller factor, $\Delta\sigma^2$). An average distance of 1.95 Å was assigned to the Ti–O distance in anatase and all changes in the Debye–Waller factor are reported relative to anatase at room temperature. Curve fitting was performed in k-space regions 4.5–12.0 $Å^{-1}$ for ETS-10, 4.5–10.3 $Å^{-1}$ for Ti-β, and 3.3–9.1 $Å^{-1}$ for TS-1. A large glitch observed in the spectra at about 50 eV above the absorption edge was outside of the curve fitting range.

3. Results and discussion

Results from elemental analysis and nitrogen adsorption, reported in table 1, are representative of TS-1, Al-free Ti-β, and ETS-10 molecular sieves. Local structural information associated with the Ti sites in the materials is derived from UV and X-ray absorption spectra. The energy of the UV absorption edge of TS-1 is con-

Table 1
Chemical compositions and micropore volumes of Ti molecular sieves

Sample	Ti/(Ti + Si) atomic ratio	Micropore volume [a] ($cm^3\,g^{-1}$)
TS-1	0.024	0.206
Ti-β	0.024	0.258
ETS-10	0.170	0.123

[a] Determined from dinitrogen adsorption at $P/P_0 = 0.3$.

sidered excellent evidence for incorporation of Ti atoms into the tetrahedral framework sites of silicalite [3]. As shown in fig. 1, the UV absorption threshold of Ti-β is close to that of TS-1, suggesting that Ti atoms are coordinated tetrahedrally in the molecular sieve frameworks of both materials. The UV absorption threshold of ETS-10, a molecular sieve containing Ti atoms coordinated octahedrally, is shown in fig. 1 for comparison. The 30 nm shift in UV absorption energy of ETS-10 clearly demonstrates the difference between Ti environments (octahedral and tetrahedral) in molecular sieves.

Additional structural information in the vicinity of the Ti atoms can be obtained from X-ray absorption spectroscopy at the Ti K edge. When Ti atoms are bonded in geometric configurations that lack an inversion center, such as a tetrahedron, the near-edge region contains a pre-edge feature almost as intense as the absorption edge. However, the electronic transition that accounts for the pre-edge feature in tetrahedrally-coordinated Ti compounds is disallowed in octahedrally-coordinated compounds [12]. The Ti K-edge spectra of ETS-10 and anatase (TiO_2) presented in fig. 2 clearly illustrate this point since both materials contain Ti in octahedral coordination. The small pre-edge features in fig. 2 result from local distortions in the oxygen octahedra surrounding the Ti atoms.

The Ti K-edge spectra of TS-1 and Al-free Ti-β in various environments are presented in figs. 3 and 4. A major difference between the spectra of the dehydrated

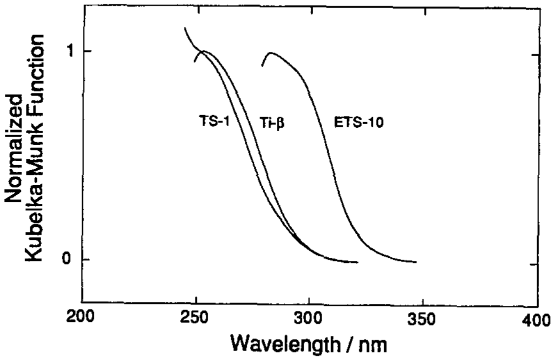

Fig. 1. Normalized absorption spectra derived from UV diffuse reflectance spectroscopy of TS-1, Ti-β and ETS-10.

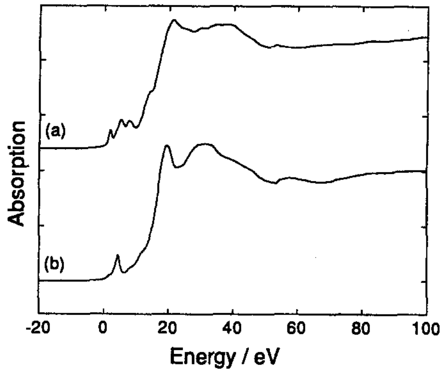

Fig. 2. Ti K-edge XANES collected at RT for (a) anatase TiO_2 and (b) ETS-10.

TS-1 and Ti-β (figs. 3a and 4a) and the spectrum of ETS-10 is the position and intensity of the pre-edge feature. As indicated in table 2, the small pre-edge feature for ETS-10 is shifted relative to the large pre-edge peaks for TS-1 and Ti-β to higher

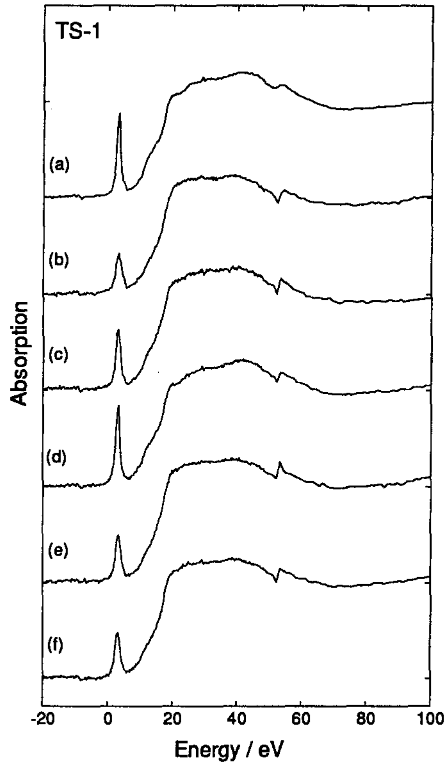

Fig. 3. Ti K-edge XANES for TS-1 collected at RT after various treatments: (a) dehydrated; (b) in presence of ethanol; (c) after methanol exposure and purged with He; (d) sample in (c) after calcination in He at 573 K; (e) sample in (d) in presence of 2-propanol; (f) after 2-propanol exposure and purged with He.

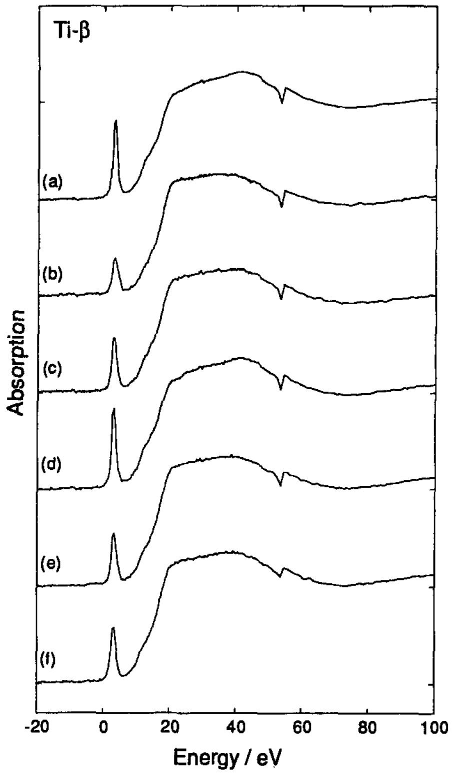

Fig. 4. Ti K-edge XANES for Ti-β collected at RT after various treatments: (a) dehydrated; (b) in presence of methanol; (c) after methanol exposure and purged with He: (d) sample in (c) after calcination in He at 573 K; (e) sample in (d) in presence of 2-propanol; (f) after 2-propanol exposure and purged with He.

energy by 1 eV. Earlier works have reported shifts in energy of the pre-edge feature as a function of Ti coordination [13]. For example, the pre-edge peak for Ti phthalocyanine, a material with Ti in square pyramidal coordination, is shifted by 1 eV to higher energy than the pre-edge feature of Ba_2TiO_4, a material with Ti in tetrahedral coordination [14]. The difference between the near-edge structure of ETS-10 and either TS-1 or Ti-β is clearly due to the coordination state of the Ti atoms in samples. Since the spectra of the calcined, dehydrated samples in figs. 3a and 4a are virtually identical, Ti-β must have Ti atoms in sites that closely resemble the tetrahedral sites of TS-1.

We also examined the effect of adsorbed alcohols on the near-edge structures of TS-1 and Al-free Ti-β. Figs. 3b and 4b present the near-edge spectra of the samples in the presence of vapor-phase methanol, whereas figs. 3c and 4c show the effect of purging the cell with helium after methanol exposure. The position, intensity, and full width at half maximum of the pre-edge peaks are reported in table 2. The spectra of both TS-1 and Ti-β are altered identically (within experimental error) by the treatments. The pre-edge peaks decreased in intensity and broadened

Table 2
Summary of pre-edge peak characteristics

Sample	Position[a] (eV)	Intensity[b] (%)	FWHM[c] (eV)
TS-1, dehydrated	3.5	87	1.5
TS-1, MeOH exposed	3.5	42	2.2
TS-1, MeOH, He purge	3.5	60	1.8
TS-1, calcined in He	3.5	84	1.5
TS-1, 2PrOH exposed	3.5	47	2.0
TS-1, 2PrOH, He purge	3.5	46	2.0
Ti-β, dehydrated	3.5	81	1.5
Ti-β, MeOH exposed	3.5	39	2.2
Ti-β, MeOH, He purge	3.5	55	1.8
Ti-β, calcined in He	3.5	84	1.5
Ti-β, 2PrOH exposed	3.5	54	1.9
Ti-β, 2PrOH, He purge	3.5	57	1.9
ETS-10	4.5	23	2.0

[a] Refers to shift in energy from the first peak in Ti K edge of Ti foil (±0.2 eV).
[b] Calculated from peak intensity divided by absorption step.
[c] Full width at half maximum (0.2 eV).

by 0.7 eV when the samples were exposed to methanol, but partially recovered to their initial values after purging with helium. Calcination of the samples at 573 K in flowing He regenerated the original spectra as shown in figs. 3d and 4d. The same experiments were performed with the samples exposed to 2-propanol vapor and the results are shown in figs. 3e,f and 4e,f as well as table 2. Again, the spectra for TS-1 and Ti-β were affected similarly by adsorption of an alcohol. In summary, we found that adsorption of two different sized alcohols onto the samples profoundly altered the near-edge spectra of TS-1 and Ti-β, and that both materials were altered in exactly the same way.

The EXAFS data associated with ETS-10, dehydrated Ti-β, and dehydrated TS-1 are given in fig. 5. Radial structure functions derived from EXAFS of ETS-10 and anatase are compared in fig. 6a. The large peak in the Fourier transforms (FT) between 1 and 2 Å corresponds to the average Ti–O distance in each sample. The curve-fit in fig. 6b was used to calculate structural parameters for ETS-10 reported in table 3. The Ti–O interatomic distance in ETS-10 was found to be 2.00 ± 0.01 Å, which is 0.05 Å longer than the Ti–O distance in anatase. The calculated coordination number of ETS-10 ($N = 5.5$) was within 10% of the known value of 6. Interestingly, the change in Debye–Waller factor relative to anatase was negative, indicating that the distances in ETS-10 are more uniform than in anatase. Each Ti atom in ETS-10 has 2 Ti and 4 Si neighbors in its second shell which accounts for the second major peak in the FT. Similarly, the smaller peaks at longer distances in the FT of anatase result from higher shell Ti–Ti contributions. The

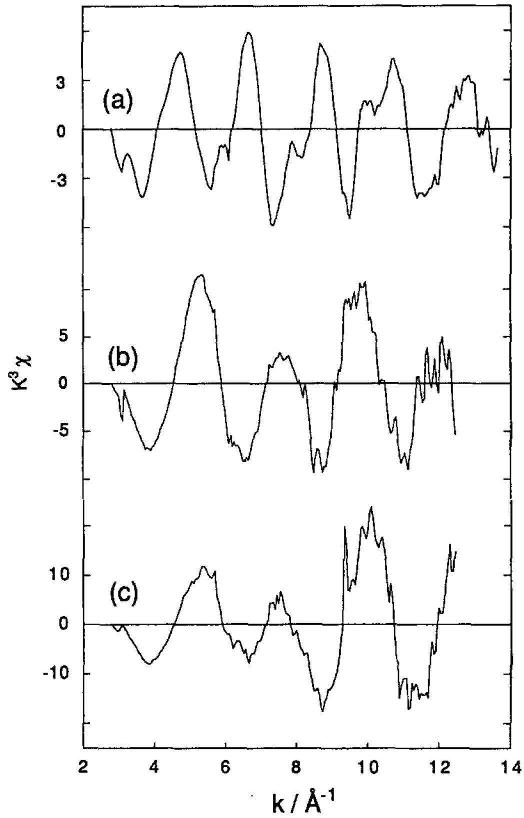

Fig. 5. The $k^3\chi$ EXAFS functions for samples (a) ETS-10; (b) dehydrated Ti-β; (c) dehydrated TS-1.

long Ti–O distance in ETS-10 found by EXAFS is not unusual and compares well with Ti–O distances in silicate minerals containing octahedrally-coordinated Ti atoms [15].

The Fourier transforms of the EXAFS for TS-1 and Al-free Ti-β, with and without adsorbed methanol, are shown in figs. 7 and 8. The peak below 1 Å results from a baseline residue in the EXAFS function and was not included in the calculation of structural parameters. A summary of the parameters derived from EXAFS analysis of the samples is presented in table 3. Since the coordination number and Debye–Waller factor are highly correlated, the limited range in k-space (~ 6 Å^{-1}) used for curve fitting of samples with low Ti loadings resulted in significant errors in N and $\Delta\sigma^2$. The error in Ti–O interatomic distance, however, is still estimated to be ±0.01 Å. Thus, we will limit our discussion of the structure to the Ti–O distance for these two samples. In both dehydrated samples, the Ti–O interatomic distance was calculated to be 1.80 ± 0.01 Å which is identical to the value found earlier for TS-1 [2]. The same Ti–O distances for the two samples confirms the conclusion from XANES that Ti atoms in aluminum-free Ti-β occupy regular tetrahedral sites in the zeolite framework. Earlier work in our laboratory demonstrated that Ti

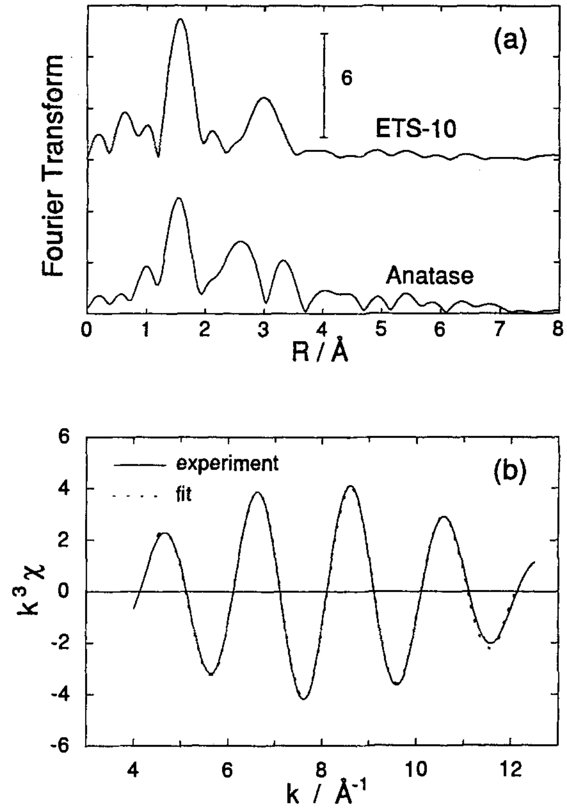

Fig. 6. Results from analysis of Ti K-edge EXAFS for ETS-10 and anatase; (a) comparison of radial structure functions (not corrected for phase shifts) derived from Fourier transforms of $k^3\chi(k)$ functions and (b) Fourier filtered EXAFS function and resulting curve fit used to calculate the Ti–O structural parameters for ETS-10.

atoms in amorphous mixed oxides of TiO_2–SiO_2 also reside in tetrahedral sites [16]. Adsorption of methanol onto the zeolite samples lengthens the average Ti–O bond distance to about 1.83 Å. A similar result was found for ammonia adsorption onto TS-1 and was attributed to the expansion of the Ti coordination sphere to

Table 3
Structural parameters derived from Ti K-edge EXAFS

Sample	R_{Ti-O} (Å)	N	$\Delta\sigma^2$ (Å^2)	ΔE_0 (eV)
ETS-10	2.00	5.5	−0.0029	+4
TS-1, dehydrated	1.80	5.7	−0.0093	+5
TS-1, MeOH exposed	1.83	5.2	−0.0102	+3
Ti-β, dehydrated	1.81	6.7	−0.0055	+3
Ti-β, MeOH exposed	1.83	4.2	−0.0079	+2

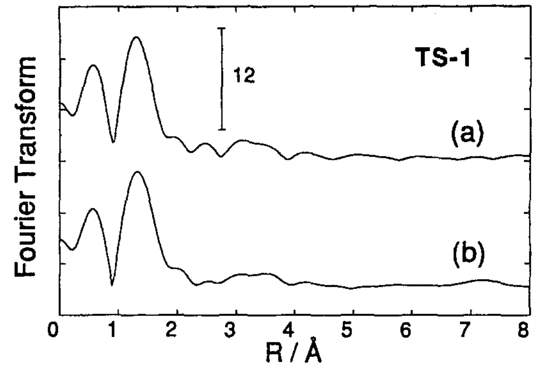

Fig. 7. Comparison of radial structure functions (not corrected for phase shifts) for TS-1 (a) dehydrated and (b) in the presence of methanol.

include the four framework oxygens and adsorbed ammonia [3]. It was also speculated that the expansion of the coordination sphere of Ti by NH_3 causes Ti to move outward from its regular framework position which lengthens the Ti–O bonds. In our case, the adsorbed alcohol may actually dissociate and form an adsorbed alkoxy species and a neighboring hydroxyl species. The coordination sphere of Ti would still include only four oxygens but in non-regular tetrahedral configuration. This scheme could account for both the lengthening of the average Ti–O bond and the decrease in the intensity of the pre-edge peak upon alcohol adsorption. Otherwise, the altered spectra may simply result from expansion of the Ti coordination sphere as described above. Unfortunately, we cannot discriminate between the two models based on the results presented here.

The structural results determined by X-ray absorption spectroscopy of aluminum-free Ti-β are different from earlier studies on aluminum-containing Ti-β that utilized the same technique [7]. For example, the pre-edge peak for the aluminum-

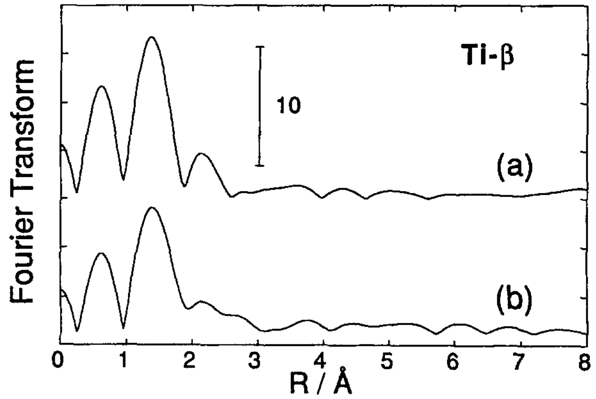

Fig. 8. Comparison of radial structure functions (not corrected for phase shifts) for Ti-β (a) dehydrated and (b) in the presence of methanol.

free sample has about 28% greater intensity than the peak for the aluminum-containing sample. In addition, the average Ti–O bond distance in the material without aluminum is 0.05 Å shorter than the material containing aluminum. An explanation for the effect of framework aluminum on the structure of Ti sites in Ti-β is unknown at this time.

4. Conclusions

Results from UV reflectance spectroscopy, in situ EXAFS and in situ XANES indicate that Ti sites in aluminum-free Ti-β are structurally similar to the tetrahedral sites in TS-1 and are very different from the octahedral sites in ETS-10. In addition, X-ray absorption spectroscopy of the materials in the presence of alcohols was not able to distinguish between the Ti sites in TS-1 and aluminum-free Ti-β. Comparison of our structural results to earlier published work indicates that the Ti sites in aluminum-free Ti-β are altered from those in aluminum-containing Ti-β.

Acknowledgement

Acknowledgements are made to the National Science Foundation for a Young Investigator Award (RJD), to the donors of the Petroleum Research Fund, administered by the American Chemical Society (ACS-PRF 28260-AC5), and to ARCO Chemical Company for support of this research. The work was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the US Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. We acknowledge ARCO Chemical Company for helpful discussions and for providing the materials used in this study.

References

[1] B. Notari, Catal. Today 18 (1993) 163.
[2] S. Pei, G.W. Zajac, J.A. Kaduk, J. Farber, B.I. Boyanov, D. Duck, D. Fazzini, T.I. Morrison and D.S. Yang, Catal. Lett. 21 (1993) 333.
[3] S. Bordiga, S. Coluccia, C. Lamberti, L. Marchese, A. Zecchina, F. Boscherini, F. Buffa, F. Genoni, G. Leofanti, G. Petrini and G. Vlaic, J. Phys. Chem. 98 (1994) 4125.
[4] C.B. Khouw, C.B. Dartt, J.A. Labinger and M.E. Davis, J. Catal. 149 (1994) 195.
[5] M.G. Clerici and P. Ingallinia, J. Catal. 140 (1993) 71.
[6] A. Corma, M.A. Camblor, P. Esteve, A. Martinez and J. Perez-Pariente, J. Catal. 145 (1994) 151.
[7] T. Blasco, M.A. Camblor, A. Corma and J. Perez-Pariente, J. Am. Chem. Soc. 115 (1993) 11806.

[8] M.W. Anderson, O. Terasaki, T. Ohsuna, A. Philippou, S.P. Mackay, A. Ferreira, J. Rocha and S. Lidin, Nature 367 (1994) 347.
[9] M. Taramasso, G. Perego and B. Notari, US Patent 4,410,501 (1983).
[10] US Patent appl. #08/329732 assigned to ARCO Chemical Technology, L.P.
[11] W.W. Wendlandt and H. Hecht, *Reflectance Spectroscopy* (Wiley–Interscience, New York, 1966).
[12] R.B. Greegor, F.W. Lytle, D.R. Sandstrom, J. Wong and P. Shultz, J. Non-Cryst. Sol. 55 (1983) 27.
[13] F. Babonneau, S. Doeuff, A. Leaustic, C. Sanchez, C. Cartier and M. Verdaguer, Inorg. Chem. 27 (1988) 3166.
[14] C.A. Yarker, P.A.V. Johnson, A.C. Wright, J. Wong, R.B. Greegor, F.W. Lytle and R.N. Sinclair, J. Non-Cryst. Sol. 79 (1986) 117.
[15] G.A. Waychunas, Am. Miner. 72 (1987) 849.
[16] Z. Liu and R.J. Davis, J. Phys. Chem. 98 (1994) 1253.