EXAFS Study of Rutile and Anatase

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Two crystallographic forms of TiO_2 (rutile and anatase) were subject to an extended x-ray absorption fine structure study at the K threshold of titanium. Data analysis was carried out by Fourier methods and curve fitting techniques. Using the theoretical phases, Ti-O bond distances of 1.93(1) Å were derived both for rutile and anatase, as compared to the crystallographic values of 1.948–1.980(1) Å (rutile) and 1.934–1.980(1) Å (anatase). The ratio of the cation coordination numbers $N_r/N_a = 1.07$ is close to the theoretical value.

Introduction

As part of a program of characterization of high yield Ziegler-Natta catalysts, we have undertaken extended x-ray absorption fine structure (EXAFS) studies of various titanium compounds with an all-chlorine or all-oxygen first coordination shell. In a preceeding paper [1] we have described our results for some titanium chlorides; here we present our results for a Ti-O first shell compound, namely TiO_2 in the polymorphic forms of rutile and anatase.

Experimental

Materials: Rutile and anatase were commercial SIBIT products (impurity level $<0.5\%$). After admixture of chemically inert and x-ray transparent BN, about 0.1 g of the powder was pressed in tabular form (1×2 cm). The TiO_2/diluent ratio was such that $\mu x \approx 2$ (including the absorption due to BN) in order to optimize contrast at the high-absorption side of the Ti K edge. The tablets were then inserted in a stainless steel frame together with a 4μ thick titanium sheet (Goodfellow Ltd., 99.5%) which was used as a reference material to the energy scale.

Data Collection: EXAFS spectra were recorded at the Synchrotron Radiation Facility (PULS) at the National Laboratories (INFN), Frascati (Italy), using the x-ray beam line. The experimental apparatus has been described previously [2] and data collection followed our standard procedures [3]. All EXAFS spectra were taken in air at room temperature, at ≈ 1.5 eV intervals over a scan range of about 1300 eV, extending up to 800 eV above the K threshold of Ti, measuring for 1 sec. each.

Data processing was carried out on a UNIVAC 1100/20 computer using a locally written program set with general graphical and mathematical routines due to B. Pianzola.

Data Evaluation: For reliable comparison of the results obtained from the two TiO_2 samples, the EXAFS spectra were extracted from the experimental absorption data μx using a uniform procedure (thus excluding bias due to the data handling [4]). At variance of the procedures of Ref. [1] and in view of the rather extended pre-edge absorption [5], the smooth absorption background $\mu' x$ was subtracted using a Victoreen fit [6]; the atomic-like contribution $\mu_0 x$ was obtained by means of a Fourier filtering technique [1, 7]. The EXAFS signal was then calculated as

$$\chi(k) = [\mu(k)\,x - \mu'(k)\,x - \mu_0(k)\,x]/\mu_0(k)\,x\,.$$

In converting the absorption data from the photon energy E_x to the wave vector of the outgoing electron

$$k = [(E_x - E_0)\,2\,m/\hbar^2]^{1/2}$$

the reference energy E_0 was fixed, with an arbitrary but uniform choice, at the inflection point of the K-edge of titanium (4983.8(2), 4983.1(2) and

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4964.5 eV for rutile, anatase and metallic titanium, respectively, with the latter being used for calibration of the energy scale [1]). Figs. 1 and 2 report the EXAFS signal $\chi(k)$ vs k for the two samples.

According to the single scattering theory, the EXAFS signal [8–10] is given by

$$\chi(k) = \frac{1}{k} \Sigma_i A_i(k) \sin[(2kR_i + \Phi_i(k)],$$

where the sum is over i coordination shells, R_i is the distance of the ith shell from the absorber and $\Phi_i(k)$ the phase shift of the photoelectron caused by the potential of the absorbing and backscattering atoms. The amplitude envelope A_i is given by

$$A_i(k) = (N_i/R_i^2) \exp(-2\sigma_i^2 k^2) F_i(k),$$

where N_i is the number of atoms at distance R_i and σ_i^2 the Debye-Waller like term. In this expression the amplitude $F_i(k)$ is given by

$$F_i(k) = f_i(\pi, k) \exp(-2R_i/\lambda),$$

where $f_i(\pi, k)$ is the backscattering factor [11] for each of the N_i neighbouring atoms in the ith shell and λ is the mean free path of the photoelectrons [12].

The EXAFS signals, weighted by k for compensating amplitude reduction [12], were Fourier transformed from k to R space according to

$$FT(R) = \left(\frac{1}{2\pi}\right)^{1/2} \cdot \int_{k_{\min}}^{k_{\max}} W(k)\, k\, \chi(k) \exp(-2ikR)\, dk$$

with $k_{\min} = 3.9$ and $k_{\max} = 13.8$, and $W(k)$ being a gaussian window function [1]. As may be seen from Figs. 3 and 4, the modulus of $FT(R)$ of anatase shows a strong peak in correspondence to the first shell and several weak higher shell contributions. On the other hand, $|FT(R)|$ of rutile shows three peaks which may be attributed to the first Ti-O coordination sphere at about 1.96 Å, Ti-Ti distances at 2.959 Å and Ti-O contributions at about 3.50 Å.

The first peak of each radial distribution function was then backtransformed (FT^{-1}) in the

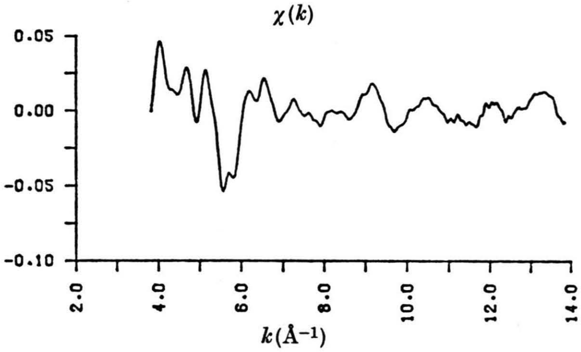

Fig. 1. EXAFS signal $\chi(k)$ vs k for rutile.

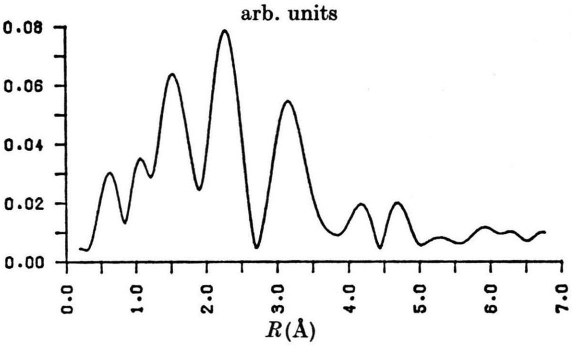

Fig. 3. Modulus of the Fourier transform for EXAFS signal of rutile.

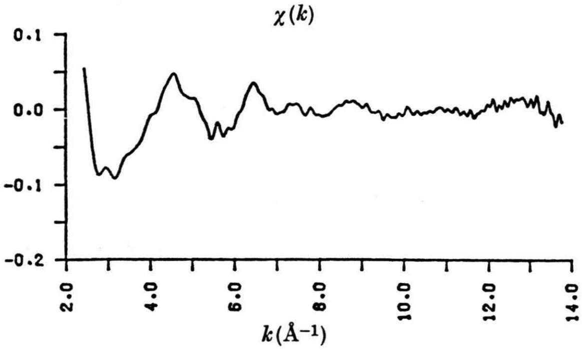

Fig. 2. EXAFS signal $\chi(k)$ vs k for anatase.

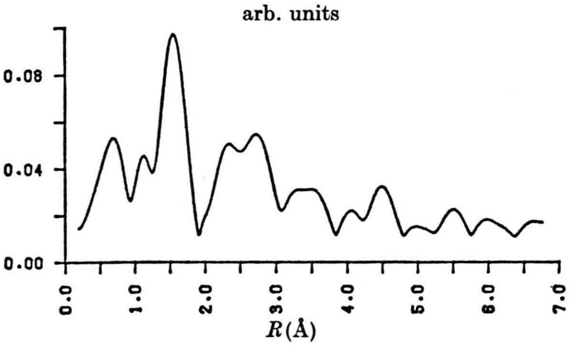

Fig. 4. Modulus of the Fourier transform for EXAFS signal of anatase.

range 1.20—1.90 Å for rutile and 1.26—1.90 Å for anatase, according to

$$\chi_1(k) = \sqrt{\frac{2}{\pi}}\, k^{-1}\, W(k)^{-1} \cdot \int_{R_1}^{R_2} FT(R)\exp(2ikR)\,\mathrm{d}R\,.$$

Results and Discussion

Distance information was derived by first dividing the backtransformed signal $\chi_1(k)k$ by $|FT^{-1}|$ to obtain the sinusoidal term

$$\varphi_1(k, R) = \sin[2kR_1 + \Phi_1(k)]$$

and by subsequent least-squares fitting of $\varphi_1(k, R)$. The phase shift function $\Phi_1(k)$ was parametrized in the form

$$\Phi(k) = a_0 + b_0 - \pi + (a_1 + b_1)k + (a_2 + b_2)k^2 + (a_3 + b_3)/k^3$$

according to [13]. During the fitting the phase parameters were constrained to the theoretical values [14] (Table 1). This restricts the variables to R_i and ΔE_0, where the latter is required for the definition of

$$k' = (k^2 + 0.262467\,\Delta E_0)^{1/2}$$

with k being defined as above and ΔE_0 corresponding to an energy shift with respect to a previously reported value [10, 13]. This fitting procedure is rapid and avoids strong correlations between the parameters [4], which may compromise their physical significance. The maximum number of independent parameters, N_{free}, in a fitting procedure has been given by Eisenberger [15] as

$$N_{\text{free}} \approx 0.6\,\Delta R\,\Delta k\,,$$

where ΔR is the Fourier filter length $(R_2 - R_1)$ and Δk the interval in k space in the fit. The fitted functions for rutile and anatase are reported in Figs. 5 and 6 ($k_{\min} = 4.5$, $k_{\max} = 12.5$). Comparison of the resulting parameter values with the crystallographic Ti-O distances [16, 17] shows excellent agreement (Table 2). The ratio of the titanium coordination numbers in the two samples has been

$a_0 + b_0 - \pi$	2.73440
$a_1 + b_1$	$-$ 1.36929 Å
$a_2 + b_2$	0.03393 Å^2
$a_3 + b_3$	39.05040 Å^{-3}

Table 1. Fitted theoretical absorber and backscatter phase parameters for Ti-O.

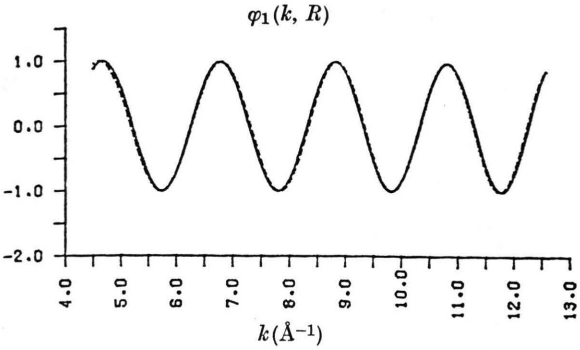

Fig. 5. Curve fitting analysis for rutile: fit (---) of the experimental signal $\varphi_1(k, R_1)$ vs. k (—).

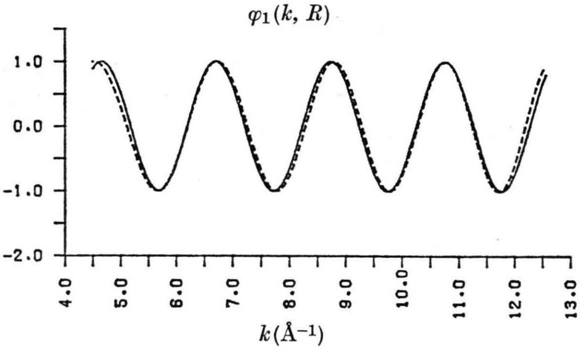

Fig. 6. Curve fitting analysis for anatase: fit (---) of the experimental signal $\varphi_1(k, R_1)$ vs. k (—).

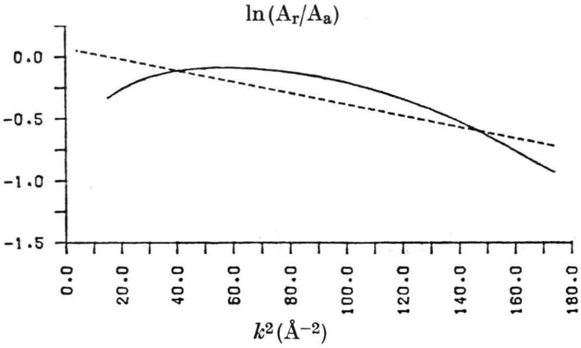

Fig. 7. Logarithmic ratio of $|FT^{-1}|$ for rutile and anatase vs k^2 (—) with fit (---) for the definition of the coordination number of anatase ($N_{\text{rutile}} = 6.0$).

Table 2. Results of fitting $\sin[2kR_1 + \Phi_1(k)]$.

Sample	ΔE_0 (eV)	R (Å)	Cryst. value (Å)	Ref.
Rutile	$-$ 16.0	1.93 (1)	1.948 (1) (4 ×) 1.980 (1) (2 ×)	[16]
Anatase	$-$ 13.4	1.93 (1)	1.934 (1) (4 ×) 1.980 (1) (2 ×)	[17]

calculated according to the procedure proposed by Sayers et al. [18] from the moduli of FT^{-1}:

$$\frac{A_r(k)}{A_a(k)} = \frac{N_r}{N_a}\frac{R_a^2}{R_r^2}\exp[-2(\sigma_r^2-\sigma_a^2)k^2].$$

The value of $N_a = 6.45$ is obtained for $N_r = 6$ by plotting

$$\ln(A_r(k)/A_a(k)) \text{ vs } k^2.$$

The discrepancy with respect to the theoretical value is within the error limits of the method [5] and derives probably from the strong overlap between the first shell in rutile with the background peak and second shell, which leads to distorsions in the A_r term. The calculated value of

$$\Delta\sigma^2 (= \sigma_r^2 - \sigma_a^2) = -0.0022 \text{ Å}^2.$$

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