

## Enhancement of the ETS-10 Titanosilicate Activity in the Shape-Selective Photocatalytic Degradation of Large Aromatic Molecules by Controlled Defect Production

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**Abstract:** In recent times, it has been shown that the microporous ETS-10 titanosilicate can be used as a shape-selective photocatalyst for the decomposition of aromatic molecules (*Chem. Commun.* **2001**, 2131). Its actual use on practical grounds is however discouraged by its too low activity, when compared with that of TiO<sub>2</sub> photocatalysts. In the present work, we show how an ad hoc mild treatment with HF enhances the activity of ETS-10 toward the photodegradation of large aromatic molecules that are unable to penetrate inside the zeolitic pores, such as 2,5-dichlorophenol, 2,4,5-trichlorophenol, 1,3,5-trihydroxybenzene, and 2,3-dihydroxynaphthalene (DHN). The photoactivity of the acid-treated materials is comparable or even greater than that of the nonselective TiO<sub>2</sub> catalyst. Moreover, the enhancement of the photoactivity is accompanied by a remarkable parallel increase of the shape selectivity, particularly toward DHN ( $k_{\text{DHN}}/k_{\text{P}} = 127$ , where P = phenol). A complete characterization (by means of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, ultraviolet–visible spectroscopy, and X-ray absorption spectroscopy techniques) of a set of ETS-10 samples which have undergone a progressively severe HF treatment allows us to propose an explanation of the photocatalytic activity and selectivity of the modified materials.

### 1. Introduction

Heterogeneous photocatalysts based on TiO<sub>2</sub> metal oxides are extensively studied, especially for their application in organic synthesis,<sup>1,2</sup> or in the abatement of hazardous pollutants in water, in air, or on solid surfaces.<sup>3–6</sup> The initiation step of the photocatalytic process consists in the generation of electron–hole pairs upon irradiation of the material with a convenient light source (with an energy greater than its band gap). These photoformed charge carriers can migrate rapidly to the surface of the solid, where they are trapped: electrons produce the reduction of surface Ti(IV) ions into Ti(III), while holes interact (in the presence of water) with formation of •OH and TiO• radical species. These radical species can then initiate the oxidative photodegradation of several organic substrates.

When TiO<sub>2</sub> is used as the photocatalyst, photodegradation processes are nonselective, and thus, the possibility to degrade at will only a given component from a mixture is precluded. Therefore, preparation of selective photocatalysts is an interesting and intriguing goal, as it opens new potential fields of application where nonselective TiO<sub>2</sub> catalysts cannot be used. This can be the case for separation processes, or the selective elimination of (pollutant) molecules from a mixture.

To our best knowledge, only two papers have been published up to now on selective photocatalysts. Ghosh-Mukerji et al.<sup>7</sup> have reported recently the innovative preparation of selective TiO<sub>2</sub> composite photocatalysts, containing specific molecular sites for the recognition of the target molecule in the vicinity of titanium dioxide. Following an alternative approach,<sup>8</sup> we have shown that selective photocatalysis can be obtained through the use of proper molecular sieves (ETS-10) as shape-selective heterogeneous photocatalysts. The activity of the titanosilicate ETS-10<sup>9</sup> has been known for a few years.<sup>8,10,11</sup> This activity is

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**Table 1.** Most Relevant Properties of the ETS-10 Samples Prepared

sample	HF/H <sub>2</sub> O concn (wt %)	relative crystallinity <sup>a</sup> (%)	Ti ← O–O LMCT intensity (Kubelka–Munk)	amt of exposed Ti(IV) <sup>b</sup> (mol of Ti/g of solid)	amt of exposed Ti(IV) (% Ti total)
ETS-10/0		100	1.4	$0.8 \times 10^{-5}$	0.5
ETS-10/1	1 <sup>c</sup>	98	2.6	$1.5 \times 10^{-5}$	0.9
ETS-10/2	2 <sup>d</sup>	96	3.5	$2.1 \times 10^{-5}$	1.2
ETS-10/8	8 <sup>e</sup>	95	3.9	$2.3 \times 10^{-5}$	1.3

<sup>a</sup> Determined by XRD. <sup>b</sup> Determined from the curve in Figure 4b. <sup>c</sup> [HF] = 0.56 M. <sup>d</sup> [HF] = 1.13 M. <sup>e</sup> [HF] = 4.52 M.

local environment of Ti species induced by the HF treatment and by interaction with H<sub>2</sub>O<sub>2</sub>.

To test the photoactivity of the modified ETS-10 samples, two sets of reactions have been investigated: (i) the competitive photodegradation of 4-chlorophenol (CP), 2,5-dichlorophenol (DCP), and 2,4,5-trichlorophenol (TCP) and (ii) competitive photodegradation of phenol (P), 1,3,5-trihydroxybenzene (THB), and 2,3-dihydroxynaphthalene (DHN). The results obtained in each set of experiments using as photocatalyst a commercial TiO<sub>2</sub> sample (Degussa P25) have also been considered for comparison. In both sets of reactions, molecules with different steric hindrance (relative to the diameter of the ETS-10 channels) have been used to check for possible shape-selectivity effects.

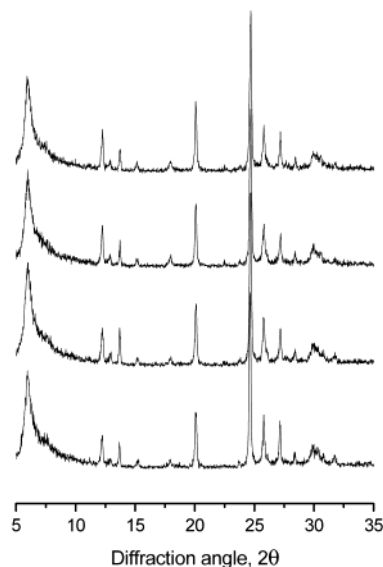
## 2. Experimental Section

The starting (Na,K)-ETS-10 was a commercial sample kindly supplied by Engelhard (Iselin, NJ); its external surface area was 21 m<sup>2</sup> g<sup>-1</sup> (*t*-plot volumetric measurements with N<sub>2</sub> made with a Micromeritics ASAP 2010 instrument). TiO<sub>2</sub> was a commercial Degussa P25 sample (surface area about 50 m<sup>2</sup> g<sup>-1</sup>). All the organic compounds (P, CP, DCP, TCP, THB, and DHN) were purchased from Aldrich and used as received.

Acid treatments of the ETS-10 samples were performed with diluted aqueous solutions of HF of different concentrations, ranging from 1% to 8% (wt %). In separate experiments, portions of the solid sample (1.5 g) were contacted with 5 mL of the H<sub>2</sub>O/HF solution for a few seconds, then quickly diluted with a large excess of distilled water, filtered under a vacuum, and thoroughly washed with H<sub>2</sub>O. These samples will be hereafter denoted ETS-10/*X*, where *X* stands for the concentration (wt %) of HF in the aqueous solution used for the treatment; ETS-10/0 will thus be the untreated (starting) ETS-10 material, which was used here as a reference. In Table 1, the samples prepared and their nomenclature and most relevant properties are reported.

Elemental analysis was performed by measuring the X-ray fluorescence yield of Si, Ti, Na<sup>+</sup>, and K<sup>+</sup> on a Philips PW 1404/10 instrument equipped with a double Sc, Mo anode. The Na<sup>+</sup> and K<sup>+</sup> contents were also cross-checked by atomic absorption measurements (ICP-MS instrument equipped with a Perkin-Elmer Elan 5000 mass spectrometer). The amount of H<sup>+</sup> in the HF treated samples was calculated as the difference between the stoichiometry expected value (two monovalent cations per Ti atom) and the measured Na<sup>+</sup> and K<sup>+</sup> contents. The results obtained showed that the Si/Ti molar ratio progressively decreases from 4.92 (ETS-10/0) to 4.39 (ETS-10/8). These changes are accompanied by a progressive ion exchange of Na<sup>+</sup> (and K<sup>+</sup>) by H<sup>+</sup>, reaching a maximum fraction, [H<sup>+</sup>]/[Na<sup>+</sup> + K<sup>+</sup> + H<sup>+</sup>], of 0.45 in the most severely treated sample, Na<sup>+</sup> being the most exchanged cation.

Powder XRD (Cu Kα radiation) of the samples were performed with a Siemens D5000 diffractometer. The high-resolution micrographs were obtained on a JEOL JEM 2000 EX transmission electron microscope equipped with a top entry stage. DRUV-vis spectra were recorded using a Perkin-Elmer Lambda 19 spectrophotometer, in the range



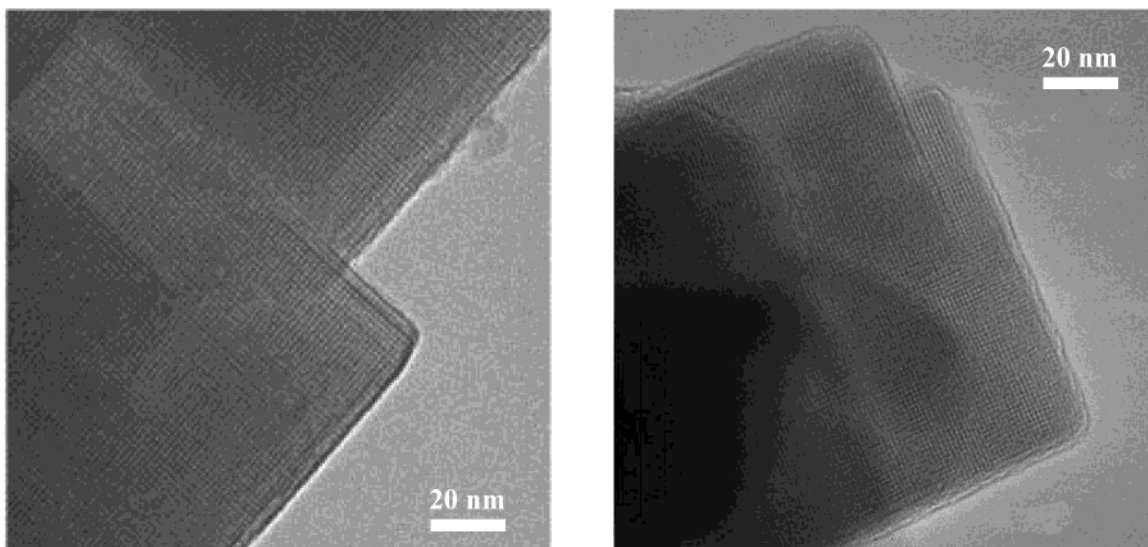
**Figure 2.** X-ray diffractograms (Cu Kα radiation) of, from bottom to top, ETS-10/0, ETS-10/1, ETS-10/2, and ETS-10/8 samples.

5000–4000 cm<sup>-1</sup>. The measurements were taken under incipient wetness conditions. XAFS spectra were obtained in the transmission mode, at the EXAFS13 beam line of the DCI storage ring (operating at 1.85 GeV with a typical current of 300 mA) at LURE laboratories in Orsay (France), using air-filled ionization chambers for both incident and transmitted beams. For both detectors the gas pressure has been optimized ad hoc for each sample, maximizing the measured current within the linearity region of the device. The incident beam was monochromatized using a double-crystal Si(111) with a sampling step of 2.0 eV and an integration time of 2.0 s per point. The energy/angle calibration was performed using a Ti foil, and crystals were detuned up to 1/2 of the rocking curve to avoid harmonics. For each sample four equivalent XAFS spectra were acquired under the same experimental conditions and averaged before Fourier filtering.

For photocatalytic reactions, the irradiation of the single species was carried out on 5 mL of aqueous suspension containing  $1 \times 10^{-4}$  M organic compound and 1 g dm<sup>-3</sup> catalyst, using a 1500 W xenon lamp (Solarbox, CO.FO. MEGRA, Milan, Italy) simulating AM1 solar light and equipped with a 310 nm cutoff filter. The total photonic flux in the 310–400 nm range and the temperature in the cell have been kept constant for all the experiments at  $1.35 \times 10^{-5}$  einstein min<sup>-1</sup> and 323 K, respectively. The disappearance of the primary compound and the intermediate evolution with time were followed using high-performance liquid chromatography (HPLC). A Rheodyne injector, a RP C18 column (Lichrochart, Merck, 12.5 cm × 0.4 cm, 5 μm packing), a high-pressure two-pump gradient (Merck Hitachi L-6200 and L-6000 pumps), and UV-vis detection (Merck Hitachi L-4200) were used. The irradiation of the two equimolar mixtures of the three molecules (i.e., CP/DCP/TCP and P/THB/DHN) was done by using the same conditions as before, and using concentrations of all molecules of  $1 \times 10^{-4}$  M.

## 3. Results and Discussion

**3.1. X-ray Diffraction.** X-ray diffraction was used to check the effect of the acid treatments on the crystallinity of the samples prepared as described in the previous section. Figure 2 shows the X-ray diffractograms (Cu Kα radiation) of the acid-modified samples, as well as that of the parent (unmodified) ETS-10 sample. As can be seen from the diffractograms all samples exhibit high crystallinity and are analogous to those reported before.<sup>12,13</sup> No additional peaks belonging to other phases are observed.



**Figure 3.** HRTEM micrographs (200 kV, magnification  $2 \times 10^5$ ) of the samples ETS-10/0 (left) and ETS-10/8 (right).

The relative crystallinities of the acid-treated samples (Table 1) have been evaluated following standard procedures.<sup>27</sup> The crystallinity of the starting material (ETS-10/0 sample) was arbitrarily assumed to be 100%, and the other values were obtained by considering their relative intensity (peak area) of the diffraction lines near  $2\theta = 20^\circ$  and  $25^\circ$ . Silicon (Aldrich, 99.99%) was used as the internal standard. The relative intensities reported in Table 1 are averaged values for several independent measurements of the same sample. According to these values, it can be concluded that in all cases the acid treatment conditions used to modify the ETS-10 samples are mild enough to preserve their crystalline structure. Only a small reduction of the relative crystallinity (less than ca. 5% for the most severely treated sample) of the samples is observed as a consequence of the acid treatment.

**3.2. Textural and Morphologic Modification of ETS-10 upon Acid Treatment.** The textural characterization of the starting and acid-modified samples was performed by adsorption/desorption isotherms of  $N_2$  at 77 K. The  $t$ -plot method was used to evaluate the external surface area ( $S_{\text{ext}}$ ). The results obtained show a significant increase of  $S_{\text{ext}}$  (the associated uncertainty being within  $2 \text{ m}^2 \text{ g}^{-1}$ ), which moves from  $21 \text{ m}^2 \text{ g}^{-1}$  for the starting sample up to  $27\text{--}30 \text{ m}^2 \text{ g}^{-1}$  for the acid-modified samples. The differences observed between the series of acid-treated samples are, however, within the experimental accuracy, and no significant trend among them can be appreciated. No mesopore formation has been observed on HF-treated samples.

Morphologic characterization of ETS-10 samples, prior to and after the acid treatments, was performed by means of SEM and HRTEM. The SEM micrographs obtained are not reported for brevity. The starting material shows cubic-like crystallites ca. 250–300 nm in size. No significant differences are observed as a consequence of the acid treatment: both the morphology and dimensions of the crystallites remain basically unmodified. These results indicate that the modifications produced by the acid treatment occur at a level beyond the detection limit of the SEM, in agreement with the relatively low loss of crystal-

linity measured by XRD. This means that the induced modifications have nanoscale dimensions (defects).

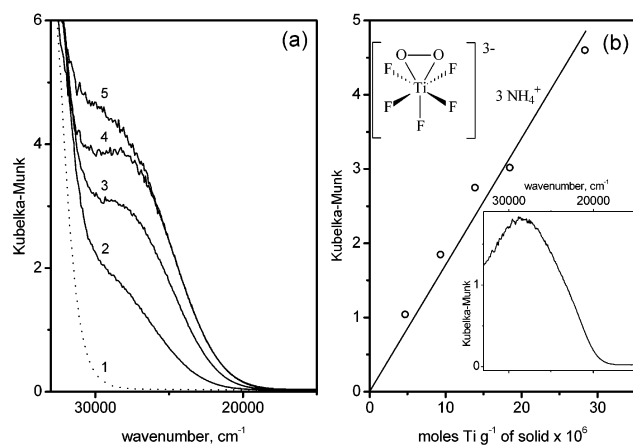
A better detail of the morphology of the microcrystals can be gained from the HRTEM images shown in Figure 3. The starting ETS-10 sample presents a well-defined pattern of interference fringes. The terminations of the crystals are sharp and well defined, and when terraces are present, they are neat and have well marked steps. After the acid treatment, mild erosion of the crystallite borders is observed, occurring on an atomic scale. The pattern of interference fringes is still well defined, which indicates that the HF treatment has not caused the ETS-10 structure to collapse through the formation of a high concentration of internal defects. This is shown for the case of ETS-10/8, but the same effect was also observed for the other samples.

On the basis of these results, it is concluded that HF mainly corrodes the external surfaces, with appearance of new TiOH groups (vide infra). Finally, it is worth mentioning that, during the HRTEM measurements, a different stability of the ETS-10 samples under the electron beam was observed. In the adopted experimental conditions, the starting ETS-10/0 sample was found to be stable for ca. 1 min of exposure to the electron beam (before the interference fringes start to disappear), while the acid-treated samples started to lose considerably their crystallinity after ca. 30–45 s. This fact can be explained by the differences in the amount of adsorbed water; possibly proton exchange accompanying acid modification results in more strongly adsorbed water in the modified samples that can cause instability under the electron beam.

**3.3. DRUV–Vis Spectroscopy: Titration of the Exposed Ti Sites with  $H_2O_2$ .** It is well-known that exposed Ti(IV) centers (for instance, in TS-1<sup>28</sup>) readily interact with  $H_2O_2$  to give colored yellow-orange surface species absorbing at ca.  $26000\text{--}28000 \text{ cm}^{-1}$ . For this reason, we have used hydrogen peroxide as a titrant molecule of the accessible Ti centers (in the form of exposed TiOH groups) in the ETS-10 samples prepared by acid treatment.

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**Figure 4.** (a) DRUV-vis spectra of the sample ETS-10/0 wetted with pure water (spectrum 1, dotted line) and with an aqueous solution of  $\text{H}_2\text{O}_2$  (spectrum 2). Spectra 3–5 correspond to the samples ETS-10/1, ETS-10/2, and ETS-10/8 wetted with an aqueous solution of  $\text{H}_2\text{O}_2$  (same conditions as those of spectrum 2). (b) Calibration curve obtained from solid samples impregnated with aqueous solutions of the coordination complex  $(\text{NH}_4)_3[\text{Ti}(\text{O}_2)\text{F}_5]$ : one of the spectra obtained is shown in the inset. See the text for details.

Figure 4a shows the DRUV-vis spectra obtained for the ETS-10 samples wetted with an aqueous solution of hydrogen peroxide (30% v/v). For comparison, also the spectrum corresponding to the parent ETS-10/0 sample wetted with pure distilled water is presented (spectrum 1, dotted line).

The band at  $28000\text{ cm}^{-1}$ , observed for the starting (untreated) ETS-10/0 sample after interaction with  $\text{H}_2\text{O}_2$  (spectrum 2 in Figure 4a), is attributed to a ligand-to-metal charge-transfer transition (LMCT) of a peroxo-type species formed at exposed titanium sites on the pristine sample. This assignment is confirmed by the fact that a similar band is not present in the spectrum of the ETS-10/0 sample contacted with  $\text{H}_2\text{O}$  (spectrum 1, dotted line).

The LMCT transition band at  $28000\text{ cm}^{-1}$  is present with intensification in the spectra of the acid-treated samples (spectra 3–5); i.e., the more severe the acid treatment, the greater the intensity of the LMCT transition band (see Table 1). A neat and progressive increase of its intensity is observed on going from the sample ETS-10/0 (spectrum 2) to ETS-10/2 (spectrum 4). It is therefore clear that, as a consequence of the acid treatment, the quantity of accessible titanium sites is increased as compared to that in the starting material. Since the UV-vis spectra were taken under incipient wetness conditions ( $\text{H}_2\text{O}_2$  always being in excess), the intensity of the LMCT band is directly related to the concentration of titanium centers exposed.

We notice however that in the sample ETS-10/8 (spectrum 5) only a moderate intensity increase of the LMCT band is observed (from 3.5 to 3.9, Kubelka–Munk), which is accompanied by a blue shift of the maximum, now at  $29000\text{ cm}^{-1}$ . These facts seem to indicate that the Ti species present in the sample ETS-10/8 that are able to interact with hydrogen peroxide are somewhat different in nature from those present in the other acid-treated samples. We will see in the following that this fact can have consequences on the photocatalytic performance of the material (section 3.6).

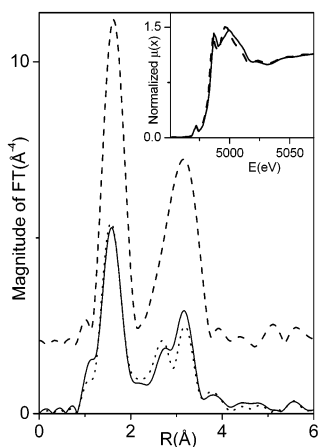
To quantify the amount of titanium centers exposed in the ETS-10 samples, the titanium-peroxo coordination complex  $(\text{NH}_4)_3[\text{Ti}(\text{O}_2)\text{F}_5]$  was used as a reference to construct a

calibration curve (absorbance of the peroxo-titanate vs the concentration of Ti(IV)). To this end, aqueous solutions of  $(\text{NH}_4)_3[\text{Ti}(\text{O}_2)\text{F}_5]$  of known concentration were prepared and used to impregnate weighed amounts of an inert, white solid having no titanium (silicalite-1). The DRUV-vis spectra of these samples were then recorded in the same conditions adopted for the ETS-10 samples, and the values of the absorbance (Kubelka–Munk) at  $28000\text{ cm}^{-1}$  used to construct the calibration curve shown in Figure 4b. The choice of this complex as a reference has some advantages: (i) the complex is soluble in water, thus allowing the simple preparation of reference samples with a known titanium content (expressed as moles of titanium per gram of solid); (ii) the UV-vis spectra of the  $(\text{NH}_4)_3[\text{Ti}(\text{O}_2)\text{F}_5]$ /silicalite-1 samples show an absorption band at  $28000\text{ cm}^{-1}$ , which is very similar to that present in the ETS-10 samples upon interaction with  $\text{H}_2\text{O}_2$ . The LMCT bands originating from fluorine ligands occur at much higher frequencies. The most severe limitation associated with the use of  $(\text{NH}_4)_3[\text{Ti}(\text{O}_2)\text{F}_5]$ -impregnated samples as references lies in the assumption that the extinction coefficient of the LMCT transition of the reference compound is essentially identical to that of peroxo species formed on ETS-10 samples upon interaction with  $\text{H}_2\text{O}_2$ . For this reason, the values obtained for the amounts of accessible titanium centers in the ETS-10 samples are considered to be only approximate.

With the limitation discussed above, the acid-treated ETS-10 samples were found to contain an amount of titanium ions which can interact with hydrogen peroxide ranging from ca. 0.5% to 1.3% of the whole structural titanium (the exact value depending on the treatment conditions used; see Table 1). Although the absolute values can be considered as being only approximate, they still represent an estimation of the actual order of magnitude of accessible titanium centers in the acid-modified samples. More reliable information is given by their relative values; i.e., the concentration of Ti(IV) centers that can interact with  $\text{H}_2\text{O}_2$  is increased about 2.5–3 times on passing from ETS-10/0 to ETS-10/8. The damage of the framework necessary for the formation of such a small concentration of accessible titanium ions at defective positions (involving less than 2% of the whole titanium) prevents the ETS-10 structure from collapsing, as already demonstrated by X-ray diffraction (vide supra).

**3.4. XAFS Study.** The effect of HF treatments on the local environment of Ti species is shown in Figure 5, where the Fourier transform of the XAFS spectra of the starting sample (dashed curve) and of one of the treated samples (solid curve) are compared. The XAFS spectrum of the as-prepared ETS-10/0 is rather complex and cannot be trivially divided into single first- and second-shell signals, due to the nonequivalence of the Ti–O–Si and Ti–O–Ti bonds and due to the presence of strong multiple scattering contributions caused by the near collinearity of the Ti–O–Ti bonds.<sup>29</sup> This means that any attempt to use this spectrum to derive quantitative results from the EXAFS spectra of the acid-treated ETS-10 samples is precluded. On qualitative grounds we observe a strong modification of the EXAFS signal. The strong reduction of the signal after the acidic treatments is not attributable to a loss of coordination around Ti but to a remarkable heterogeneity of

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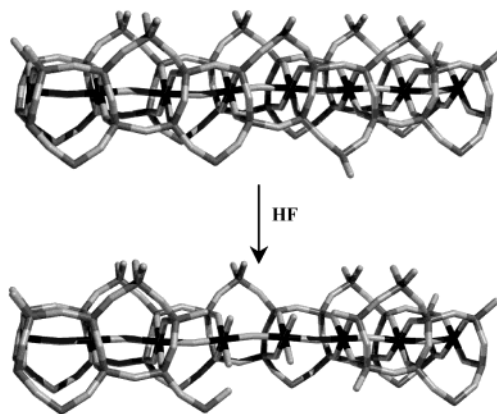
**Figure 5.** Phase-uncorrected,  $k^3$ -weighted Fourier transform of the EXAFS spectra of ETS-10/0 (dashed line), ETS-10/8 (solid line), and ETS-10/8 in interaction with  $\text{H}_2\text{O}_2$  (dotted line). The inset reports the corresponding near-edge structure for ETS-10/0 (dashed line) and ETS-10/8 (solid line). The XANES spectrum of ETS-10/8 in interaction with  $\text{H}_2\text{O}_2$  has not been reported, being virtually indistinguishable from that of ETS-10/8.

the Ti sites generated by HF treatment both directly (elimination of some second-shell Si neighbors) and indirectly (through a partial ion exchange of alkali-metal cations by protons). In fact, it is well-known that the heterogeneity implies a destructive interference among the EXAFS signals of the individual sites, resulting in a damping of the overall signal.<sup>30</sup> On the basis of these qualitative results, it could be inferred that the acid treatment involved a fraction of sites larger than that estimated by the titration method and in contrast with the XRD and HRTEM results. However, XANES spectra (see inset) show that both pre-edge peak and white line intensities are weakly affected by HF treatments, suggesting that the same distorted octahedral geometry of Ti sites holds before and after the acid treatments. This fact agrees with the hypothesis that Ti heterogeneity is the main cause of the reduction of the EXAFS signal. To give an explanation of the high heterogeneity probed by XAFS spectroscopy without invoking the massive creation of defects, we have to take into consideration that partial replacement of  $\text{Na}^+$  (and  $\text{K}^+$ ) by  $\text{H}^+$  is also taking place as a parallel effect of the acid treatment of ETS-10 with HF solutions (see the elemental analysis in section 2). Moreover, the IR spectra of the acid-treated samples outgassed at 523 K for 30 min (spectra not shown for brevity) show a new IR absorption band centered at  $3608\text{ cm}^{-1}$ , which has been assigned<sup>31,32</sup> to the O–H stretching mode of acid-bridged  $\text{Si}(\text{OH})\text{Ti}$  groups. Indeed, upon dosing with  $\text{NH}_3$  from the gas phase, formation of  $\text{NH}_4^+$  is clearly observed: this is further proof that the ionic exchange by  $\text{H}^+$  is occurring during the postsynthesis treatment. The interaction between the negatively charged Ti–O–Ti rows and alkali-metal cations ( $\text{Na}^+$  or  $\text{K}^+$ ) is of electrostatic nature, while a significant covalent contribution is expected when protons are present. So this ion exchange is expected to perturb strongly the Ti–O–Ti rows in first-shell Ti–O distances, second-shell Ti–Si and Ti–Ti distances, and especially Ti–O–Si and Ti–O–Ti angles. In this regard, it is worth noting

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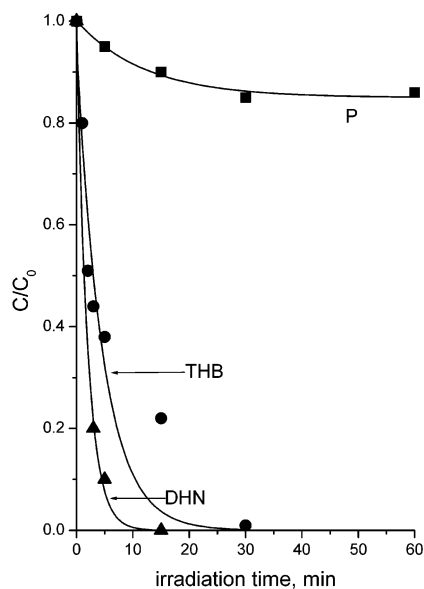
**Figure 6.** Possible mechanism of defect production on the Ti–O–Ti chains of the ETS-10 titanosilicate during the acid treatment.

that the imaginary parts of the FT of acid-treated samples with respect to those of the untreated ETS-10/0 sample (not reported for clarity) are not only reduced in intensity but also shifted in phase. This means that a destructive interference occurs between the EXAFS signal generated by unperturbed  $[\text{Ti}(\text{OSi})_4(\text{OTi})_2](\text{X}^+)_2$  units ( $\text{X}^+ = \text{Na}^+$  or  $\text{K}^+$ ) and that generated by the large variety of perturbed units, mainly by ion exchange:  $[\text{Ti}(\text{OSi})_4(\text{OTi})_2](\text{X}^+\text{H}^+)$  and  $[\text{Ti}(\text{OSi})_4(\text{OTi})_2](\text{H}^+)_2$ . These points fully justify what is observed in Figure 5, without invoking severe framework modifications (elimination of first- and/or second-shell ligands).

Conversely only a few changes have been observed upon interaction of the ETS-10/8 sample with  $\text{H}_2\text{O}_2$  (compare the solid and dotted line spectra in Figure 5). This evidence reflects the small percentage of Ti species involved in the formation of Ti–peroxo species, in agreement with UV–vis experiments (vide supra section 3.3.).

**3.5. Summary of the Characterization Studies.** Taking into account the information provided for the above-mentioned techniques (XRD, SEM, HRTEM, DRUV–vis, and XAFS), one can hypothesize that the effect of the acid treatment on the ETS-10 samples consists of the partial solution of the siliceous cover surrounding the Ti–O–Ti chains, in a process analogous to that depicted in Figure 6. This acid attack is mild enough not to alter the crystalline structure. According to the HRTEM micrographs, this attack would affect mainly the external surface of the crystals (which is also consistent with the small contact times used in the preparation of the samples). As a result of the breaking of Ti–O–Si (or Ti–O–Ti) bonds in the subsurface chains, the number of TiOH groups is expected to increase. Moreover, these titanols are not shielded, and thus, they can now interact with molecules adsorbed on the external surface and at the mouth of the channels. Actually, the amount of accessible Ti(IV) sites able to interact with  $\text{H}_2\text{O}_2$  increases progressively with the concentration of HF in the solution used for the preparation of the sample, as stated by DRUV–vis spectroscopy. The model reported in Figure 6 is also able to explain the changes observed in the EXAFS data of the acid-treated ETS-10 samples after interaction with  $\text{H}_2\text{O}_2$ : in fact the formation of a single Ti–peroxo complex in the exposed part of the Ti–O–Ti chain will perturb not only the involved Ti atom but also those adjacent to it.





**Figure 7.** Photodegradation curves of the three hydroxylated aromatic compounds over the acid-treated ETS-10/2 sample as a function of time.

In view of the results obtained and of the fact that catalytic centers are located on the external surface, it can be concluded that the zeolitic internal cavities offer a protective environment against degradation to those species that, because of their small size, can easily diffuse inside. A further confirmation of the presence of catalytic sites on the external surface is given by the fact that the degradation rate of DHN on  $\text{TiO}_2$  and on ETS-10, which have similar external surface areas, is of the same order of magnitude. The shielding effect of ETS-10 against photodegradation is particularly marked for P, which is the smallest molecule investigated, and not present for DHN, which is the only studied species whose size surely does not fit the channel size, and so it is the most degraded molecule. The ability to diffuse inside the cavities seems then the main factor determining the shape-selective degradation. However, it is worth noting that even if the previous hypothesis appears as the simplest way to explain the observed shape selectivity of ETS-10, a "pore-mouth" selectivity cannot be a priori excluded as a contributing mechanism. In fact, as photodegradation of

the organic molecules takes place at the external surface of the crystals, the ability of the organic species to accommodate in the vicinity of the pore mouth (where the Ti–O–Ti chains end) could also be important in determining its degradation rate. In this case, the mechanism of the selectivity would be different from that proposed above (in which the differences in the photodegradability are attributed only to differences in the ability to diffuse inside the channel system). Whatever the contribution of the two mechanisms, it is important to stress that in both cases we are dealing with shape selectivity.

#### 4. Conclusions

Mild postsynthesis treatments of ETS-10 molecular sieves with diluted  $\text{HF}/\text{H}_2\text{O}$  solutions are found to be a convenient method to enhance surface reactivity, as compared to that of the as-synthesized material. Mild conditions (diluted acid solutions and short contact times) have to be adopted to prevent the crystal structure of the solid from collapsing. The resulting materials show an amount of accessible titanium sites (most likely in the form of titanol groups) which is up to 2.5–3 times larger than in the parent material. Partial solution of the siliceous cover surrounding the Ti–O–Ti chains in the ETS-10 structure, with consequent breaks of Ti–O–Si (or Ti–O–Ti) linkages, seems the most likely origin of these accessible titanium sites.

The acid-treated ETS-10 samples present an enhanced activity in the photodegradation of organic molecules as compared to that of the parent ETS-10: polychlorinated and polyhydroxylated aromatic compounds have been considered here as reaction tests. More important, the increase of activity in acid-modified samples is also accompanied by a greater morphoselectivity.

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