X-ray absorption investigations on Ti-containing zeolites

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Fluorescence X-ray absorption experiments were carried out on titanium containing zeolites. The edge- and EXAFS-regions proved that the coordination of the Ti-sites of TS-1 and [Ti]ZSM-5 are similar, although no quantitative data could be obtained for the coordination numbers. EXAFS analysis of a [Li, Ti]Y zeolite, containing 12% Ti, showed that most of the titanium has a rutile-like coordination and therefore is not likely to be present as part of the framework.

Keywords: EXAFS; titanium silicalite; TS-1; [Ti]ZSM-5; [Li, Ti]Y

1. Introduction

Titanium-containing zeolites are active catalysts for a range of oxidation reactions. Examples of catalyzed reactions include the hydroxylation of phenol, the epoxidation of olefins and the oxygenation of alkanes. TS-1, a titanium silicate with the MFI topology [1] is prepared by hydrothermal synthesis [2]; other titanium-containing catalysts have been prepared by exposing the zeolite to $TiCl_4$ vapour at high temperature. It is speculated that the catalytic activity of titanium zeolites is related to the presence of isolated titanium species in the framework. Many investigations have been carried out in order to find out about the local environment of the titanium: whether it is tetrahedrally coordinated as part of the framework and whether the titanium coordination varies according to the method of preparation.

XRD [2–5], IR [2,3,5–7] and UV-Vis [7–9] experiments and more recently X-ray absorption experiments [10,11] have been carried out on TS-1. Structural information was obtained principally from the pre-edge and X-ray absorption near edge structure (XANES) regions, while the extended X-ray absorption fine structure (EXAFS) region could only be used qualitatively. The small backscattering amplitude of the oxygen in TS-1 results in a small EXAFS amplitude and therefore it is not easy to obtain reliable data.

Treating a zeolite with $TiCl_4$ vapour provides access to Ti-substituted zeolites, especially those which cannot be prepared by hydrothermal synthesis [5]. Treatment of ZSM-5 with $TiCl_4$ gave the product [Ti]ZSM-5 with a titanium content of 3% [12] which showed very similar chemical and physical properties to TS-1. Unit cell calculation showed a significant increase of the cell parameters and volume for the treated ZSM-5. EXAFS experiments were carried out in order to find out whether the coordination of titanium in TS-1 and [Ti]ZSM-5 is the same.

Titanium-containing Y zeolites cannot be directly prepared by hydrothermal synthesis, but when the zeolite [Li]Y was treated with $TiCl_4$, [Li, Ti]Y was obtained with a titanium content of 12 mol% [13] which is four times higher than in [Ti]ZSM-5. XRD, ^{29}Si MAS NMR and IR measurements indicated that dealumination of the framework occurs during titanisation. Additional weak reflections in the XRD showed the presence of a small amount of rutile but this does not account for all the titanium. This zeolite is also an active catalyst for the hydroxylation of phenol and so EXAFS experiments were carried out in order to locate the titanium in the structure.

2. Experimental

2.1. EXAFS

The X-ray absorption spectra were measured at the Synchrotron Radiation Source (SRS) in Daresbury (UK), with the synchrotron ring operating at an electron energy of 2 GeV and a current of 100–250 mA. Since the TS-1 and [Ti]ZSM-5 samples contained only 2.5–3% titanium, they were measured in fluorescence mode. The samples were pressed into self-supporting wafers which were mounted in an EXAFS cell at an angle of 45° to the incoming beam. The fluorescence-EXAFS spectra were measured on EXAFS station 8.1, using a Si(111) monochromator. For the detection of the fluorescence radiation, a solid state detector operating with 12 semiconductor elements was used. The count rate was between 2500 and 3500 counts/s for each element and the counting time was increased during a scan to improve statistics. 2×10^5 counts were accumulated at the beginning and 3×10^6 counts at the end of the spectra by adding seven scans.

As the [Li, Ti]Y contained 12 mol% titanium it was possible to measure this sample in transmission mode. The anatase and Ti-foil reference compounds were also measured in transmission mode. The sample and the reference compounds were mixed with graphitic carbon and pressed to self-supporting wafers which were mounted in a transmission EXAFS cell [14]. The measurements were done on station 7.1 of the SRS. In all experiments the monochromator was detuned to 50% of the maximal intensity in order to eliminate higher harmonic radiation. Each sample was measured in a helium atmosphere at liquid nitrogen temperature.

2.2. DATA EVALUATION

The initial averaging of the fluorescence data was done with the program EXCAL (SRS, Daresbury). The program NEX (V1.0.32) [15], which was kindly made available to us by the Eindhoven University of Technology, was used for the data evaluation. The EXAFS functions were obtained from the X-ray absorption spectra by subtracting a victoreen curve that is fitted to the pre-edge region, followed by a cubic spline background removal. Normalisation was done by division by the apparent edge height, which is obtained by back extrapolation of the background.

Reference compounds were used in order to obtain phases and backscattering amplitudes for the fitting routines. Anatase served as reference compound for the Ti–O atom pair. Since the second shell in anatase is very well separated from its neighbour shells it was used to calculate Ti–Ti reference data. In addition to anatase, a Ti-foil was measured to obtain a Ti–Ti reference. The crystallographic data of the reference compounds are listed in table 1. In the case of Ti–Si atom pairs theoretical references (Mc Kale) had to be used because no reference compound with an isolated Ti–Si or another separated appropriate atom pair could be found. Ti–Li atomic pairs need not to be considered because Li is too weak a backscatterer. The data of the reference compounds were treated in the same way as those of the samples and the resulting EXAFS-data of the reference compounds and their Fourier transforms are presented in fig. 1.

Table 1
Crystallographic data and Fourier transform ranges for the reference compounds

Compound	Coordination	N	R (Å)	Ref.	Transformation range in k (Å^{-1})	Back transformation range in R (Å)
anatase	Ti–O	4	1.93	16	2.74–19.83	0.19–1.99
	Ti–O	2	1.98		2.74–19.83	1.99–3.03
	Ti–Ti	4	3.04			
	Ti–O	8	3.86			
Ti-foil	Ti–Ti	12	2.95	17	2.51–16.59	1.31–3.20
	Ti–Ti	6	4.13			

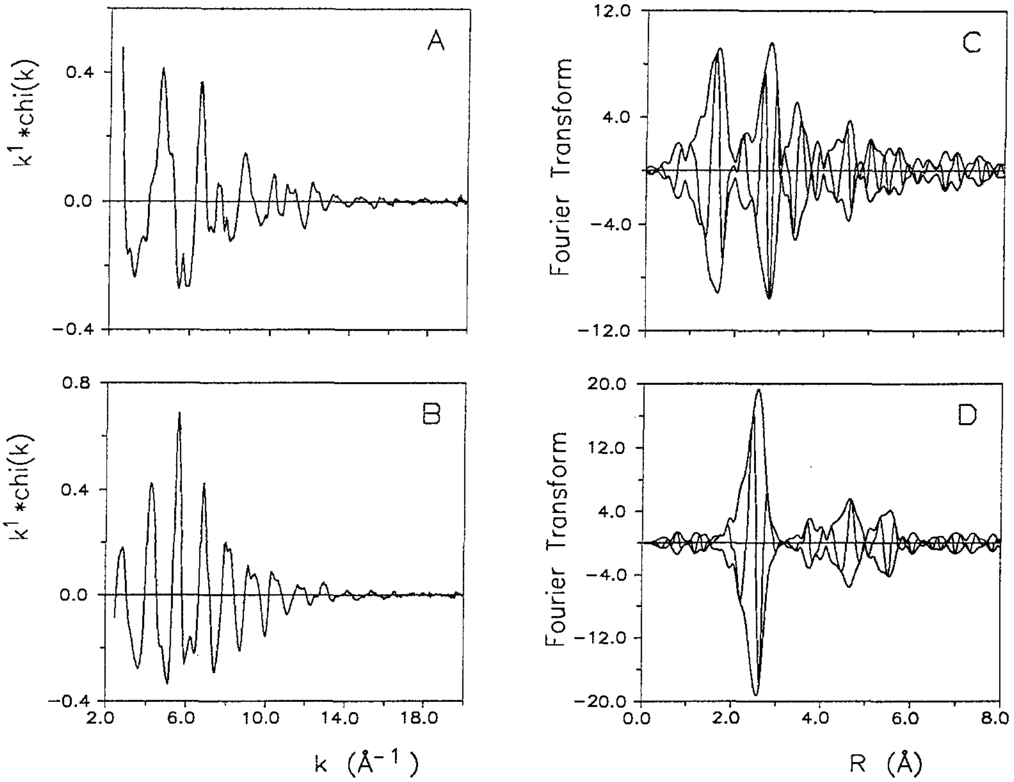

Fig. 1. EXAFS data and Fourier transforms of anatase and Ti-foil; (A) EXAFS of anatase, (B) EXAFS of Ti-foil, (C) k^3-weighted Fourier transform of anatase, (D) k^3-weighted Fourier transform of Ti-foil.

2.3. ZEOLITE CHARACTERISATION

The samples were characterized by X-ray diffraction (XRD), ^{29}Si and ^{27}Al MAS NMR, N_2 and Ar adsorption, IR and elemental analysis. The results for TS-1 and [Ti]ZSM-5 are summarized in table 2, results for zeolite Y in table 3.

3. Results

The pre-edge and the XANES regions of the normalised absorption spectra are given in fig. 2. The pre-edge absorptions stem from 1s to 3d transitions and are good indicators for the chemical environment of the absorbing atom. Behrens et al. [10,18], Waychunas [19] and Babonneau et al. [20] have measured many Ti-containing compounds with oxygen neighbours of different coordination geometry. They showed that only a pre-edge absorption which is almost as high as the edge step is a good indication for tetrahedral coordination. From a

Table 2
Characterisation results for ZSM-5 and [Ti]ZSM-5

Zeolite	XRD	BET (N_2)	Elemental analysis ICP (mol%)	
H-ZSM-5	$a = 20.111(6)$ Å $b = 19.916(6)$ Å $c = 13.401(4)$ Å unit cell vol. 5367 Å^3	surface area: 388(7) m^2/g	SiO_2 AlO_2	0.9615 0.0385
[Ti]ZSM-5	$a = 20.16(1)$ Å $b = 19.96(1)$ Å $c = 13.447(8)$ Å unit cell vol. 5415 Å^3	surface area: 357(7) m^2/g	SiO_2 AlO_2 TiO_2	0.937 [a] 0.0375 0.0260

[a] Under-determined: after addition of HF and H_2SO_4 to the titanium-zeolite powder the mixture was kept by 353 K for two days so that all the zeolite would dissolve, thus a loss of Si in form of SiF_4 was inevitable.

fitting procedure applied to the pre-edge structure of TS-1 Behrens et al. concluded that the coordination sphere of Ti consists of a mixture of tetrahedral, square pyramidal and octahedrally arranged oxygen atoms [18]. The smeared out shape of the XANES also indicated a combination of different geometries.

Table 3
Characterisation results for LiY and [Li, Ti]Y

Zeolite	XRD	Argon absorption	IR peak position (cm^{-1})	Elemental analysis AAS (mol %)	
LiY	$a = b = c =$ 24.607(1) Å volume = 14900(2) Å^3	surface area: 739(4) m^2/g micropore volume: 0.316 cm^3/g	1011.6 793.7 716.5 581.5 458.1	Li Na SiO_2 AlO_2	0.1103 0.0666 0.5922 0.2309
[Li, Ti]Y	$a = b = c =$ 24.502(5) Å volume = 14709(9) Å^3	surface area: 595(3) m^2/g micropore volume: 0.226 cm^3/g	1023.2 794.6 718.4 583.4 461.9	Li Na SiO_2 AlO_2 TiO_2	0.1043 0.0594 0.520 [a] 0.1935 0.1210

[a] See table 2.

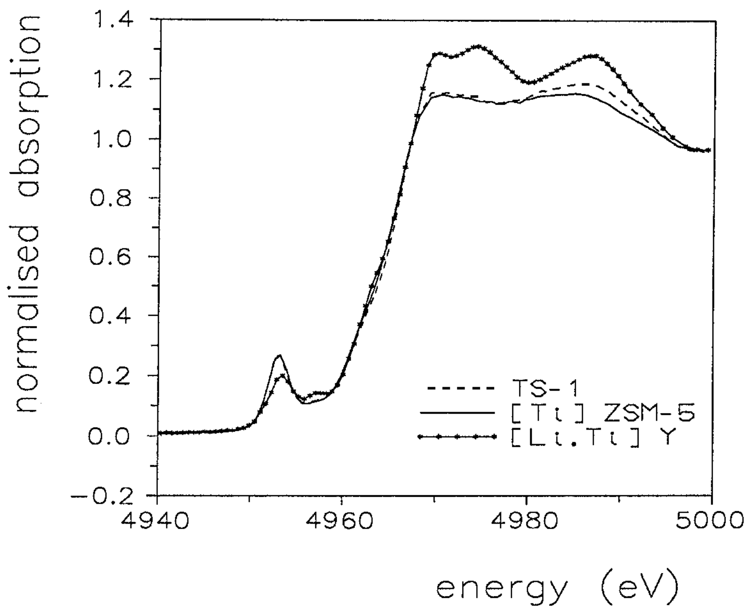

Fig. 2. Normalized pre-edge and XANES-range of the absorption spectra of TS-1 (dotted line), [Ti]ZSM-5 (straight line) and [Li, Ti]Y (line with symbols).

The pre-edge and XANES region of TS-1 and [Ti]ZSM-5 match almost perfectly. This is a good indication for a similar structure, which is further substantiated by the similarity of the Fourier transforms of the EXAFS of the two samples. In fig. 3 the raw EXAFS data and the k^1-weighted Fourier transforms for TS-1 and [Ti]ZSM-5 are given. Both transforms show a peak at 1.85 Å (phase corrected) of similar size, which belongs to the first Ti–O distance. While there are no additional peaks in [Ti]ZSM-5, there are small peaks in TS-1 at longer distances. Neither the Fourier transform of [Ti]ZSM-5, or that of TS-1 show any peaks between 3 and 4 Å which could be assigned to Ti-neighbours. Apparently the Ti atoms in these samples are well separated from each other and no TiO_2 particles are present. As already reported by Behrens et al. [18], it is very difficult to obtain a good fit for the EXAFS-spectrum of TS-1. The same is valid for [Ti]ZSM-5. It is therefore not possible to give coordination numbers for the shells of our samples. The first shell coordination number could be estimated to be between 5 and 6. The coordination distances are approximately 0.1 Å shorter than in the anatase or rutile structure. A second shell in TS- 1 may be fitted with Ti–Si references at a distance of 2.8 Å, which would indicate a large distortion of the framework, as the distance between T-atoms in an unsubstituted zeolite is approximately 3 Å. A second coordination shell was found by Behrens et al. [10,18], and assigned to a scatterer with low atomic number, but no coordination distance was reported.

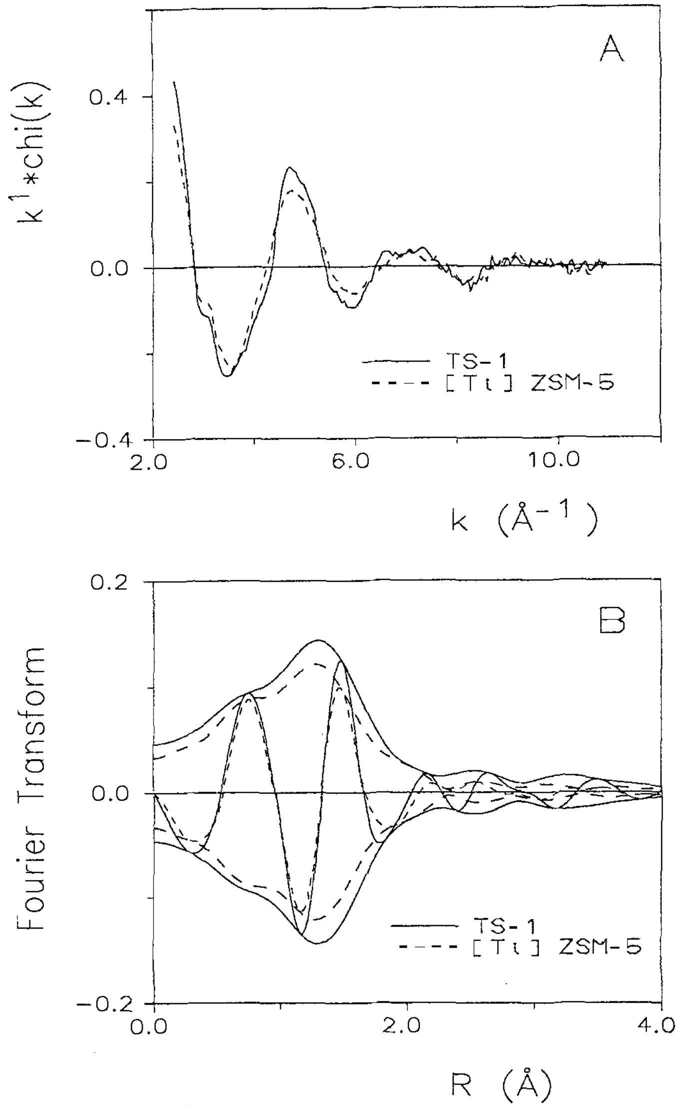

Fig. 3. EXAFS data (A) and k^1-weighted Fourier transforms (B) of TS-1 (straight line) and [Ti]ZSM-5 (dotted line).

The lack of higher coordination shells in [Ti]ZSM-5 could be explained by a large distortion of the geometry in the neighbourhood of the Ti-sites.

A different structural arrangement of titanium was found for [Li, Ti]Y, which was prepared in the same way as [Ti]ZSM-5, but which contains four times as much titanium. In addition to the Ti–O distances of the first shell, the Fourier transformation shows two further shells at 3.01 and 3.59 Å (fig. 4). These shells can be assigned to Ti–Ti distances. By comparing the k^1-weighted and k^3-weighted Fourier transforms it is evident that the third shell consists mainly of

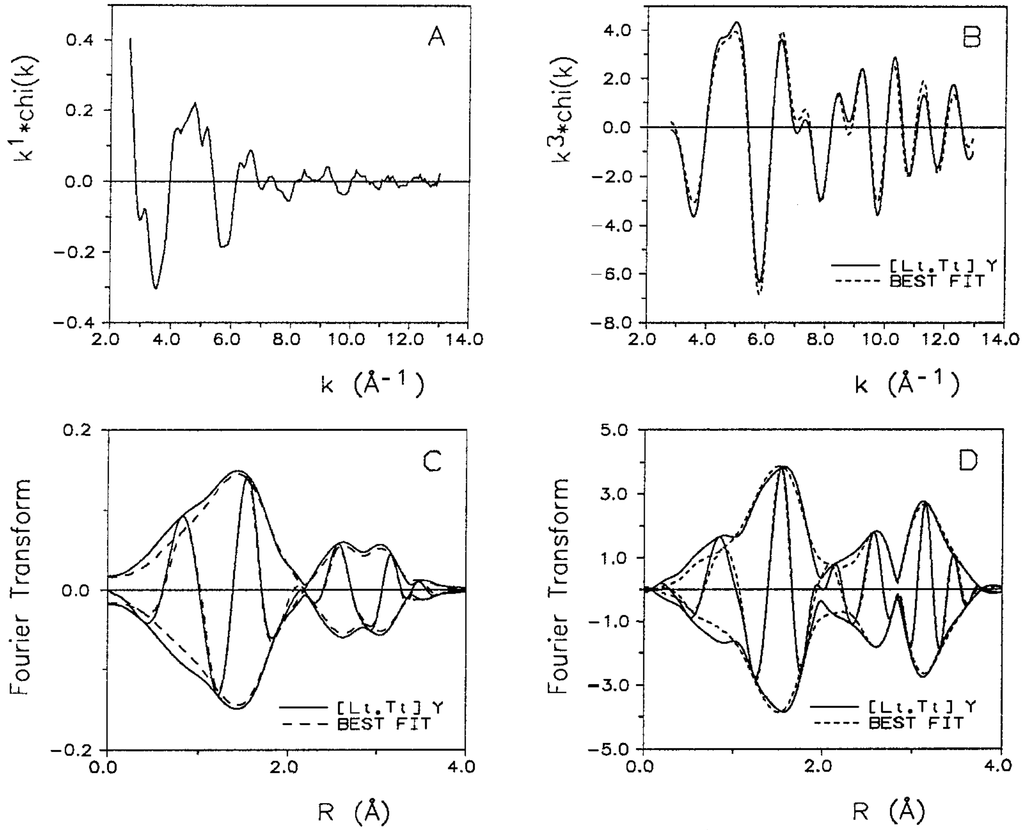

Fig. 4. EXAFS-data and Fourier transforms of [Li, Ti]Y; (A) k^1-weighted EXAFS data, (B) k^3-weighted EXAFS and best fit (dotted line), (C) k^1-weighted Fourier transform of filtered data and best fit (dotted line), (D) k^3-weighted Fourier transform of filtered data and best fit (dotted line); range of filtering $k = 2.82–12.93$ Å^{-1}, $R = 0.28–3.7$ Å.

strongly backscattering atoms, because it is drastically enhanced relative to the first shell. The situation is less clear for the second shell, but it can be concluded that it is also made up of Ti neighbours. The amplitude obtained from back-transformation of the second peak looks very similar to that of the second shell of anatase. The fitting of this shell worked best using the backtransformation of the second shell of anatase as reference.

As in TS-1 and [Ti]ZSM-5 the first shell of [Li, Ti]Y is superposed by a peak due to truncation errors, background removal or a distance distribution of a certain extent. This leads to problems in obtaining an exact coordination number. By varying the parameters in the background subtracting procedure this peak could be almost completely reduced, but this resulted in a reduction of the first shell as well. The second and third peaks were unaffected. The distances of the second and third shell (3.01 and 3.59 Å) are in very good agreement with the distances found in rutile. Also the pre-edge and XANES

Table 4
Structural parameters obtained for Ti in [Li, Ti]Y

Back scatterer	N	R (Å)	$\Delta\sigma^2$ (10^{-4} Å^2)	ΔE (eV)
O	6.4	1.95	109	−2.8
Ti	1.5	3.01	44	−4.7
Ti	4.1	3.59	0	8.5
O	3.0	3.84	0	−1.1

spectra match well. As in rutile [10,17], there are three pre-edge maxima, the first of which can only be seen as a shoulder (fig. 2). The results of the corresponding fit of the EXAFS are given in table 4. In order to fit the second and third shell two different Ti–Ti references were applied. Since the amplitude of the backtransformation of the second shell in anatase shows the same k-dependence as the corresponding amplitude of the sample, indicating a similar environment, it was used to fit the second shell. The Ti-foil reference was used to fit the third shell of the sample.

It can be concluded that small TiO_2 particles with a rutile-like coordination of the titanium are present within the [Li, Ti]Y sample. The Ti–O distance is considerably longer than in [Ti]ZSM-5. The EXAFS signal of the TiO_2 particles is so strong that it would overshadow any signal of Ti which might be incorporated in the framework. XRD-calculation of the unit cell shows a decrease; AAS, IR and ^{29}Si MAS NMR show dealumination (table 3). Catalytic activity of [Li, Ti]Y in the oxidation of phenol is significant with very high p-selectivity. The comparison of the argon absorption measurements before and after $TiCl_4$ treatment reveals a decrease of the micropore and surface area (table 3). This indicates that the TiO_2 particles are active and propably located in the supercages of the faujasite structure. More detail about catalytic activity will be given in a further paper [13].

4. Conclusion

X-ray absorption experiments were carried out on Ti-containing zeolites. In the case of TS-1 and [Ti]ZSM-5, which have the same framework topology, the local environment of the Ti atoms was compared. These zeolites were prepared in different ways, but the similarity of chemical as well as physical properties lead to the conclusion that the Ti sites of both zeolites are equivalent.

In the Fourier transforms of the EXAFS-spectra only the oxygen neighbours of the first coordination shell can be seen. As the EXAFS signals of the zeolite samples are very weak it was not possible to determine absolute coordination numbers. For both samples it can only be estimated that they are approximately five. The lack of Ti–Ti distances indicate that the Ti atoms are well separated from each other, although it could not be proven that they are incorporated in the framework. The contribution of expected Si-neighbours in second coordination shells is too small to be detected and may be further diminished by disorder due to distortion of the Ti coordination sphere. By comparison of the EXAFS with the pre-edge structures it can be clearly seen that both methods of preparation lead to equivalent coordination of the titanium atoms.

In contrast to the zeolites with MFI structure the Fourier transform of the [Li, Ti]Y shows additional Ti-neighbour shells. From the distances of these shells it can be concluded that there is a TiO_2 phase with a rutile-like structure, which could not be detected by XRD.

The catalytic properties of TS-1 have almost invariably been related to the presence of isolated titanium species in its structure. The efficiency of hydrogen peroxide used for oxygenation on TS-1 was found to be reduced by the presence of even a small amount of TiO_2 in the anatase form [21]. Anatase is not active for oxygenation. In contrast we found that small rutile-like particles enclosed within the structure of a zeolite (Y) can catalyse oxidation reactions, such as phenol hydroxylation, with astonishing *p*-selectivity. This selectivity arises from the reduction of the inner volume due to the presence of the rutile-like particles within the supercages. Those particles are probably too small to be detected with XRD methods. Rutile is the only titanium dioxide which can be reduced to give numerous nonstoichiometric phases (e.g., Magnéli phases) and could therefore theoretically act as oxide catalyst. The full description of this catalysis work will be published in a future paper [13].

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