New Aluminosilicate and Titanosilicate Delaminated Materials Active for Acid Catalysis, and Oxidation Reactions Using H_2O_2

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Abstract: A new material of zeolitic nature, ITQ-6, has been obtained by delamination of a layered precursor of ferrierite. XRD, Ar and N_2 adsorption, and ^{29}Si and ^{27}Al MAS NMR pyridine and 2,6-di-*tert*-butylpyridine adsorption show that a delaminated material with a very high external surface area has been produced. The silicoaluminate is stable upon calcination and presents strong acid sites catalytically active and highly accessible to bulky reactants. We have also obtained by direct synthesis the titanium silicate version of the laminar precursor of ferrierite and ITQ-6. The Ti is demonstrated to be in framework positions, and in the case of the TiITQ-6 is active and selective in the epoxidation of 1-hexene with H_2O_2. The TiITQ-6 is stable and remains active upon repeated reaction−calcination processes.

Introduction

The big success of zeolites as acid and redox catalysts for processing molecules with sizes in the range 0.4−0.8 nm[1] has pushed the development of new structures with larger pores able to process more bulky reactant molecules. In this sense VPI-5[2] and Cloverite,[3] molecular sieves with pores in the range of 1.5 nm, were synthesized but, unfortunately, these structures were of little utility as catalysts. Recently, two new monodirectional zeolite structures with channels formed by 14-member rings (MR), i.e., CIT-5[4] and UTD-1,[5] have been obtained and they show good behavior as acid and redox catalysts when Al and Ti were introduced into the framework.[6,7] Even though the maximum pore dimension occurring in UTD-1 is 0.74 × 0.95 nm it is still insufficient for processing the large molecules present in the heavier oil fractions,[8] as well as for reacting many of the molecules involved in the production of fine chemicals. Therefore there is still the need for developing zeolites with larger pores.

MS-14 materials,[9] of which MCM-41 is an example, have shown the benefit of very large pores. However, these materials do not show short-range order and consequently, from the point of view of the stability and catalytic behavior, they are closer to the amorphous than to the zeolitic materials.[10]

Very recently, a new approach has been undertaken for expanding the use of zeolites to catalyze reactions involving larger molecules.[11] This involves the preparation of lamellar zeolites whose structure is subsequently delaminated, making accessible through the external surface all the potentially catalytic active sites.[12] The main difference between these types of materials and the mesoporous materials of the MCM-41 type is that in the delaminated zeolites there is short-range order and consequently the active sites are of zeolitic nature.

Up to now the only delaminated material reported has been ITQ-2, which shows outstanding adsorption and catalytic properties as an acid catalyst for large reactant molecules.[11−13] Unfortunately, even though the external surface area of ITQ-2 was above 700 $m^2 \cdot g^{-1}$, not all acid sites were accessible from the external surface since a system of 10MR sinusoidal channels was still present. Furthermore, we fail in introducing transition metals by direct synthesis and we could only produce redox catalysts via secondary synthesis by anchoring Ti on the external silanol groups.[14] The resultant materials were active and selective for epoxidation of olefins with organic peroxides but they were not active when using the more desirable H_2O_2 as oxidating agent.

We have now developed a new delaminated zeolite structure (ITQ-6) in the form of silicoaluminate (AlITQ-6) as well as in the form of silicotitanate (TiITQ-6) where the acid and redox active sites were introduced by direct synthesis, and were accessible from the external surface. Here we present the synthesis characterization and catalytic activity of Al and TiITQ-6 for acid and epoxidation reactions using H_2O_2 as oxidant.

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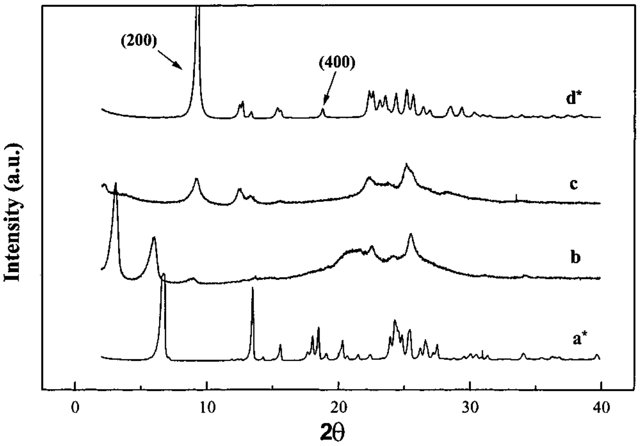

Figure 1. X-ray diffraction patterns of (a) PREFER, the laminar precursor of ferrierite, (b) PREITQ-6, the expanded material, (c) ITQ-6, a delaminated zeolite, and (d) FER, a ferrierite zeolite obtained after calcination of PREFER. Spectra reduced by a third for clarity.

Experimental Section

Materials. The ITQ-6 sample was prepared as follows: 10 g of silica (Aerosil 200, Degussa), 2.3 g of alumina (boehmite, Catapal B), 9.2 g of NH_4F (Aldrich, 98% purity), 3.1 g of HF (Aldrich, 49.8% concentration), 26 g of 4-amino-2,2,6,6-tetramethylpiperidine (Fluka, 98% purity), and 27.9 g of MiliQ deionized water were mixed in an autoclave at 448 K for 5 days. The resulting product, after it was filtered, washed 3 times with water, and dried at 333 K (PREFER), had an X-ray diffraction (XRD) pattern as shown in Figure 1a. The PREFER material was suspended in a water solution of cetyltrimethylammonium bromide ($CTA^+ Br^-$) and tetrapropylammonium hydroxide (TPA^+OH^-) and refluxed for 16 h at 368 K. The XRD pattern of the expanded material is shown in Figure 1b. Delamination was performed by placing the slurry in an ultrasound bath (50W, 40 kHz) for 1 h, maintaining a pH of 12.5 and 323 K. Finally, the solid phase was washed thoroughly with water, dried at 373 K, and calcined at 853 K for 7 h yielding ITQ-6 with an XRD pattern shown in Figure 1c.[15]

A portion of PREFER was calcined at 853 K without previous treatment to yield the ferrierite sample with an XRD pattern as shown in Figure 1d.

Apparatus and Procedures. X-ray diffraction measurements were performed with a Philips X'PERT (PN 3719) diffractometer (Cu $K\alpha$ radiation provided by a graphite monochromator) equipped with an automatic variable divergence slit and working in the constant irradiated area mode. The ^{29}Si (spinning rate of 5.5 kHz at 79.459 MHz with a 48° pulse length of 3.5 μs and recycle delay of 20 s) and ^{27}Al (spinning rate of 7 kHz at 104.218 MHz with a 9° pulse length of 0.5 μs and recycle delay of 0.5 s) MAS NMR spectra were recorded on a Varian VXR 400SWB spectrometer. Infrared spectra were measured in a Nicolet 710 FTIR by using a Pyrex vacuum cell (CaF_2 windows) and self-supporting wafers of 10 $mg \cdot cm^{-2}$. For acidity measurements, the samples were previously degassed at 673 K in a vacuum (10^{-3} Pa) overnight (background spectrum). Then pyridine (6×10^2 Pa) was admitted at room temperature and degassed at 523, 623, and 673 K for 1 h. After each treatment spectra were recorded at room temperature and the background subtracted. Analogous experiments using 2,6-di-*tert*-butylpyridine (DTBPy) as the probe molecule were also carried out in the aim of determining the external acidity of the samples.[16]

Ultraviolet spectra were performed on a Cary 5 spectrometer equipped with a Diffuse Reflectance accessory.

Catalytic Experiments. *N*-Decane and 1,3,5-triisopropylbenzene (TIPB) were cracked following the experimental procedure described elsewhere.[16] On the other hand, epoxidation of olefins was performed on TiITQ-6, following the experimental procedure used in our previous paper.[17]

Results and Discussion

ITQ-6: Preparation and Characterization. Ferrierite (FER) is a medium pore zeolite containing linked $[5^4]$ polyhedral units having intersecting channels outlined by 10MR with 0.43 × 0.55 nm and 8MR with 0.34 × 0.48 nm pore dimensions. This zeolite presents very interesting acid characteristics,[18] but the reduced pore dimensions only allow the processing of linear and monobranched olefins and paraffins. In this way it has found commercial application for the isomerization of 1-butene to isobutylene,[19] and it may also have practical interest for dewaxing and isodewaxing paraffinic feeds.

Owing to its acid properties it would be of interest to make the sites more accessible, at least in the *bc* plane, to large reactant molecules. At this point we thought of applying the preparation methodology used for obtaining ITQ-2. However, to do this, it was necessary in a first step to synthesize a laminar ferrierite, which could then be delaminated. Schreyeck and co-workers[20] synthesized an aluminosilicate named PREFER, which is a layered precursor leading, upon calcination, to a tectosilicate that was proven to be a ferrierite type zeolite.

Thus, the laminar precursor (PREFER) was synthesized here as described in the experimental part, and before drying it was expanded by using cetyl-trimethylammonium hydroxide (CTMAOH) at pH 12, achieved by using TMAOH to get the adequate charge balance between the layers. The XRD pattern of the starting laminar material as well as that of the expanded material are given in Figure 1, parts a and b, respectively. It can be seen there that CTMAOH was incorporated between the layers of the FER structure giving a d_{100} spacing of 3.6 nm. It appears then that the high bond density layers parallel to the *bc* plane, which are connected by a much lower T−O−T bond density in the interlayer, were taken apart.

At this point the expanded material was subjected to an ultrasound treatment that allows the delamination of the structure giving, after calcination at 853 K, ITQ-6 as a product. The XRD pattern of ITQ-6 (Figure 1c) compared with that of the ferrierite, obtained after calcination of PREFER at 853 K[20] (Figure 1d), shows that while the intensities of the reflections corresponding to planes (*0kl*) are basically unchanged, those corresponding to (*h*00) reflections have strongly decreased in ITQ-6, indicating a remarkable loss of order along the *a* axis. If this is so, it will indicate that the structure has been delaminated, and the resultant material is formed mostly by monolayers of the laminar precursor (PREFER), as is illustrated in Figure 2. In this scheme we can see that calcination of PREFER yields ferrierite zeolite while the swollen material can be pillared to give ITQ-36,[21] or delaminated to produce ITQ-6. It is evident from this scheme that the ITQ-6 material should present a high ratio of Q^3/Q^4 type silicon atoms where the Q^3 atoms would mainly correspond to terminal $(Si_3)SiOH$ groups pointing at the external surface of the monolayer. This is seen in Figure 3, where the ^{29}Si MAS

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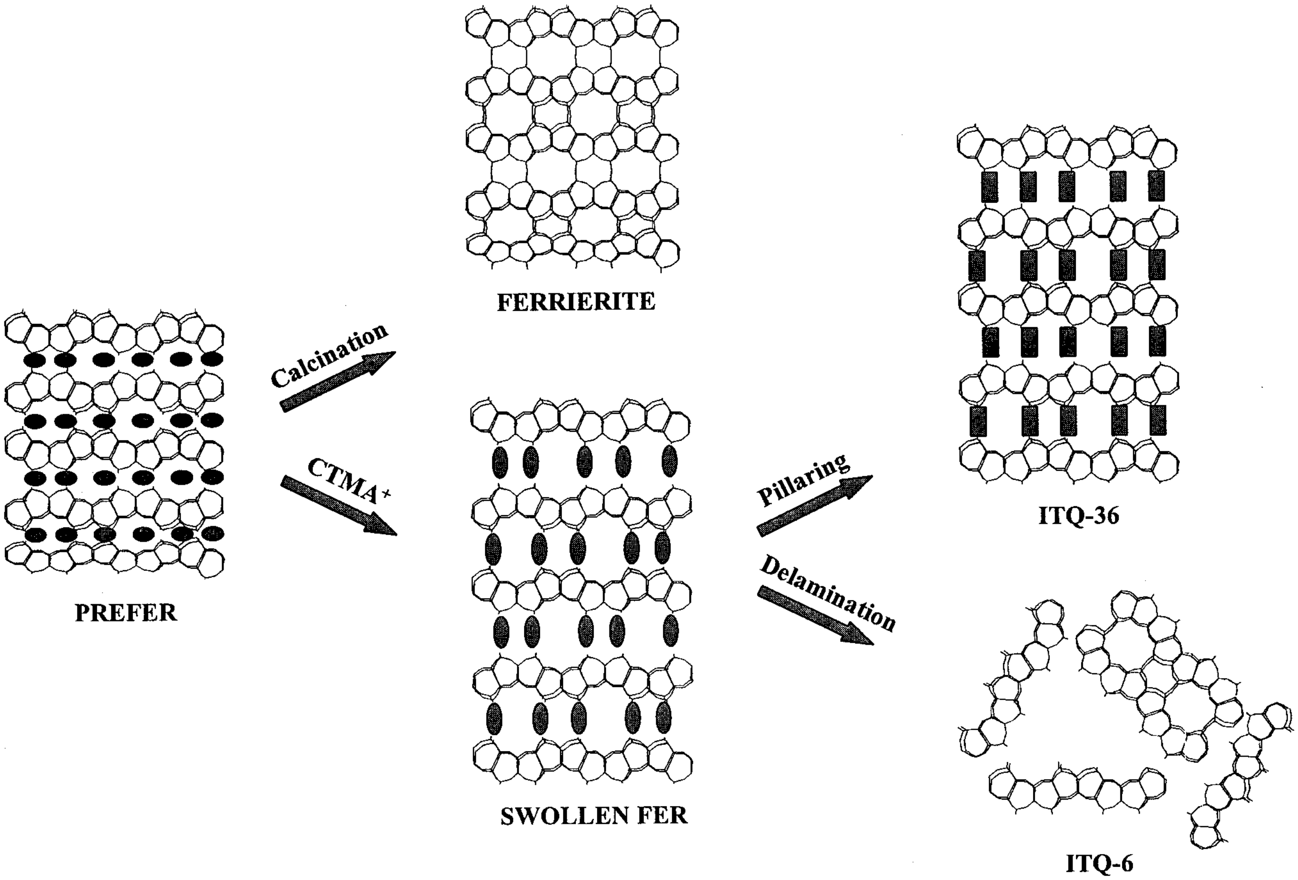

Figure 2. Schematic representation of the different materials arising from the lamellar ferrierite (PREFER).

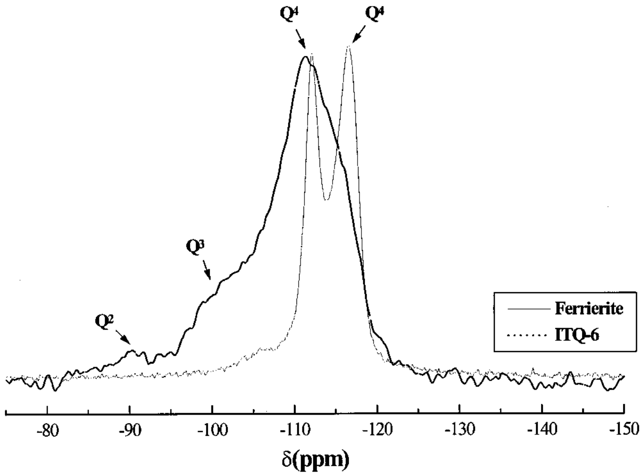

Figure 3. ^{29}Si MAS NMR spectra of (a) ferrierite (calcined PREFER) and (b) ITQ-6 (delaminated PREFER).

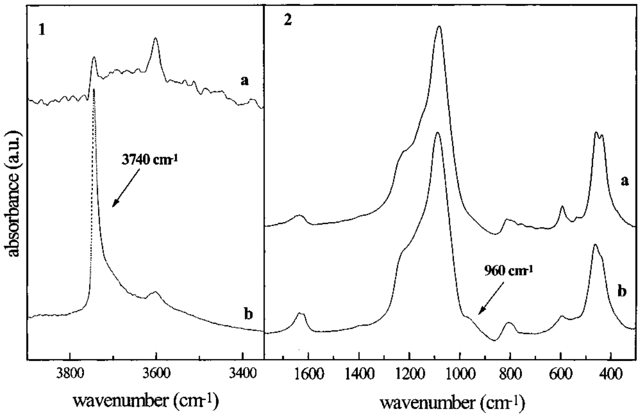

Figure 4. IR spectra in the region of (1) hydroxyl stretching vibrations and (2) framework Si−O stretching vibrations for (a) ferrierite obtained by calcination of PREFER and (b) ITQ-6 obtained by delamination of PREFER.

NMR spectra of ITQ-6 and ferrierite are compared. The spectra show the presence of Q^3 species and also the formation of Q^2 geminal groups at the vertexes of the ITQ-6 layers, and which are produced by the rupture of some of the original layers during sonication. The formation of Q^3 and Q^2 silicon atoms is also consistent with the large amount of silanol groups present in ITQ-6 and detected by IR spectroscopy (bands at 3740 and ~960 cm^{-1}) (Figure 4).

As a consequence of its structure, a delaminated material such as ITQ-6 should present a very large external surface area, with practically no microporosity. The Ar isotherms for ITQ-6 and the corresponding ferrierite are given in Figure 5 and they show that the 10MR pores present in the FER structure, which are filled at $P/P_0 \sim 5 \times 10^{-6}$, are negligible in ITQ-6. Furthermore, from N_2 isotherms, the external surface area was calculated to be 60 $m^2 \cdot g^{-1}$ for ferrierite (calcined PREFER), while that of the delaminated material is ~10 times higher (Table 1). Meanwhile, micropores have practically disappeared in this sample of ITQ-6.

Acidity and Catalytic Activity of AlITQ-6. It is important to notice that the structure of the ITQ-6 is stable after calcination at 823 K, and an important part of the aluminum is still present at tetrahedral zeolite framework positions as demonstrated by ^{27}Al MAS NMR (Figure 6). These Al generate strong acid sites as shown by adsorption−desorption of pyridine followed by IR spectroscopy. Indeed, the IR spectra given in Figure 7, show

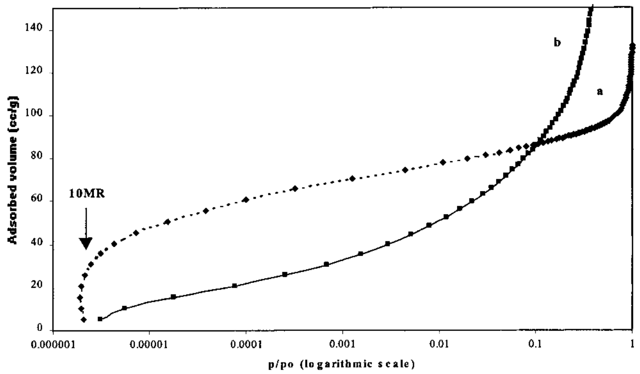

Figure 5. Argon isotherms represented as a function of log P/P_o of (a) ferrierite (calcined PREFER) and (b) ITQ-6 (delaminated PREFER).

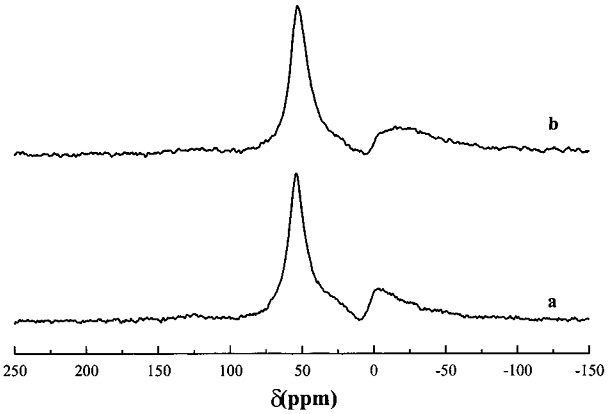

Figure 6. ^{27}Al MAS NMR spectra of (a) ferrierite (calcined PREFER) and (b) ITQ-6 (delaminated PREFER).

Table 1. Textural Characteristics: Specific Surface Area of the Different Samples from N_2 Isotherms

sample	S_{TOT} (BET)	S_{MICRO} (*t*-plot)
ferrierite	270	210
ITQ-6	618	<10

not only that the sample has Brönsted acid sites able to protonate pyridine giving pyridinium ions, but furthermore the pyridine remains adsorbed at some of the sites even after heating at 673 K under vacuum over 1 h. It has to be pointed out that when comparing the IR spectra of pyridine for PREFER and ITQ-6, it becomes apparent that during the delamination process some dealumination has also occurred resulting in a lower concentration of Brönsted acid sites in ITQ-6 (Table 2).

However, as mentioned before, even if the total number of acid sites is somewhat lower for the ITQ-6, they should be more accessible to bulky molecules than in ferrierite. This has been demonstrated by measuring the adsorption of 2,6-di-*tert*-butylpyridine (DTBPy) that certainly cannot penetrate in the 10MR pores of ferrierite.[16] The results obtained are displayed in Table 2 and show clearly that a much higher amount of DTBPy is adsorbed on ITQ-6 (90% accessibility) than on ferrierite (~5% accessibility).

Differences in the total acidity and the number of accessible Brönsted acid sites should be reflected by the catalytic activity of the catalysts for cracking *n*-decane and 1,3,5-triisopropylbenzene (TIPB). In this way, the *n*-decane molecule, which can diffuse into the 10MR pores of ferrierite, is able to interact with all acid sites regardless of their location in micropores or external surface and, in agreement with the pyridine measurements, ferrierite shows a higher catalytic activity than ITQ-6. However, when a bulkier reactant such as TIPB, which can only react at the external surface, is cracked ITQ-6 gives a higher activity (see Table 3). It is clear that through a delamination process we have generated a new zeolitic material with acid sites in the structure which are accessible to large reactant molecules owing to the very high external surface area of ITQ-6. Taking this into account it would be of interest to expand the possibilities of this material by introducing, via direct synthesis, other catalytic functions. A good candidate is titanium that, when highly dispersed in the structure with tetrahedral coordination, can introduce catalytic properties for carrying out selective oxidations.

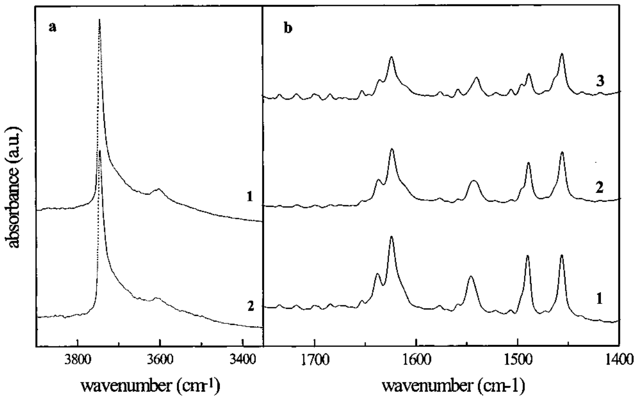

Figure 7. Acidity of ITQ-6 measured by adsorption/desorption of pyridine: (a) hydroxyl region samples calcined at 673 K (1) and after adsorption of an excess of pyridine and desorption for 1 h at 523 K (2) and (b) pyridine region after adsorption of pyridine and desorption at 523 (1), 623 (2), and 673 K (3).

Table 2. Acidity Measurements by Adsorption−Desorption of Pyridine and DTBPy Followed by IR Spectroscopy[a]

	total acidity (μmol·g^{-1} of pyridine)					
	523 K		623 K		673 K	
sample	Lewis	Brönsted	Lewis	Brönsted	Lewis	Brönsted
ferrierite	2.7	19.3	2.7	16.9	1.4	5.6
ITQ-6	8.5	9.0	6.4	6.0	5.6	5.4

	external acidity (DTPBy)	
	intensity (3365 cm^{-1})	% accessibility
ferrierite	<0.05	<5
ITQ-6	1.6	90

[a] Integrated molar extinction coefficients of adsorbed pyridine from Emeis.[28]

Table 3. Catalytic Activity of AlITQ-6 and AlFER[a]

	k (s^{-1}) × 10^2	
sample	*n*-decane	1,3,5-triisopropylbenzene
AlFER	0.25	3.5
AlITQ-6	0.21	14.0

[a] Reaction conditions: 773 K, time on stream (TOS) = 60 s, 1 bar of hydrocarbon.

Ti Containing ITQ-6 Prepared by Direct Synthesis. Up to now the only Ti-zeolites prepared by direct synthesis and which show good catalytic performance for oxidation reactions are TS-1, TS-2, and Ti-Beta.[22−24] Ti-ZSM-48 was also successfully prepared but showed no catalytic activity due to pore

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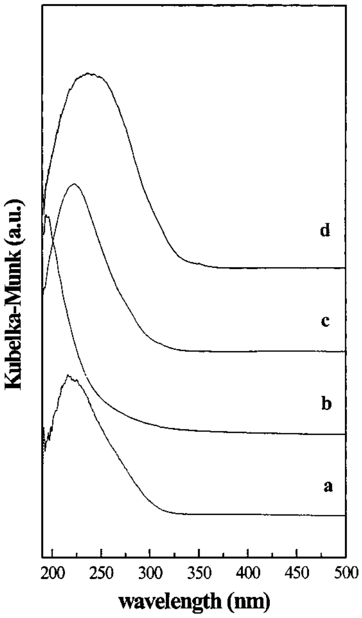

Figure 8. Diffuse reflectance spectra (UV−vis region) of TiITQ-6: (a) as synthesized (PREFER), (b) Ti−ferrierite, (c) TiITQ-6, and (d) TiITQ-6 after two reaction−calcination cycles.

Table 4. Catalytic Activity of Ti Zeolites for 1-Hexene Epoxidation[a]

sample	$X_{1-\text{hexene}}$ % of max	selectivity to epoxide	selectivity of H_2O_2	TON
TiFER	3.2	85.2	23	6
TiITQ-6	19.7	95.5	73	23
Ti−Beta	18.0	97.2	77	20
TiITQ-6 (two regeneration cycles)	17.7	93.2	56	21

[a] Reaction conditions: 16.5 mmol of olefin; 11.8 g of acetonitrile; 4.5 mmol of H_2O_2; 300 mg of catalyst; 323 K, 5 h.

Table 5. Catalytic Activity of Ti Zeolites for Norbornene Epoxidation[a]

	$X_{2-\text{norbornene}}$ % of max			selectivity to epoxide			TON
sample	2 h	5 h	7 h	2 h	5 h	7 h	(at 5 h)
TiFER	13.0	21.5	27.8	90.7	86.2	85.5	100
TiITQ-6	16.5	35.2	46.7	88.1	86.1	84.0	159
Ti-Beta	13.3	24.2	33.1	90.5	85.7	82.1	74

[a] Reaction conditions: 16.5 mmol of olefin; 11.8 g of acetonitrile; 4.5 mmol of H_2O_2; 100 mg of catalyst; 333 K.

constraints.[25] Recently[26] it has been proposed that the presence of Ti^{4+} ions tends to impede or to lower the nucleation rates in the organothermal Ti−ferrierite system, but by seeding with Si−ferrierite it was possible to prepare a Ti-containing ferrierite. Unfortunately, no catalytic activity of the sample was detected.[26] In our case, we succeeded in synthesizing directly and without adding seeds the laminar PREFER. The ultraviolet (UV) spectrum of the sample shows a single absorption band at ∼210 nm corresponding to isolated framework Ti in tetrahedral coordination (Figure 8a). This band was maintained after calcination (TiFER) (Figure 8b) and after delamination and calcination (TiITQ-6) (Figure 8c). However, in an analogous way as it occurred with the AlITQ-6, we have observed that a certain extraction of Ti from the framework has occurred during the delamination process. Nevertheless, we have prepared samples of TiFER and TiITQ-6 both with similar Ti content, i.e., 1.3 and 1.0 wt %, respectively. The samples were used as catalysts for the epoxidation of 1-hexene with H_2O_2 and the results, given in Table 4, show that TiITQ-6 is an active and selective olefin epoxidation catalyst using H_2O_2 as oxidant. Moreover, its activity is much higher than that of TiFER owing to the higher accessibility of Ti sites as a consequence of delamination of the TiPREFER structure.

To compare the activity of TiITQ-6 with that of a Ti-containing large pore tridirectional zeolite, we have synthesized a Ti-Beta with 1.3 wt % of Ti, following the procedure described previously.[27] It can be seen from the catalytic results in Table 4 that Ti-Beta and TiITQ-6 show similar activities and selectivities.

At this point, we were interested in the study of the stability of the framework Ti sites in TiITQ-6. Then, the sample used for the epoxidation of 1-hexene with H_2O_2, was calcined at 773 K and the resultant sample was characterized by UV spectroscopy and tested catalyticaly. The results in Figure 8d show that after reaction and calcination the UV spectrum still shows the band at ∼210 nm characteristic of isolated Ti^{IV}, but it also shows a small shoulder at 250−270 nm that is characteristic for the formation of some Ti−O−Ti pairs. In principle, one could expect that if some Ti comes out from the structure and agglomerates producing small TiO_2 crystallites, this should reflect in a decrease of the catalytic activity. Indeed, the regenerated catalyst shows a small decrease in activity (Table 4). However, when the catalyst sample was reused and calcined, the UV spectra remained practically unchanged, and correspondingly the catalytic activity observed in the third cycle was practically the same. It can be said then that TiITQ-6 is a reasonably stable material which is able to perform the selective epoxidation of olefins using H_2O_2 as oxidating agent. In this sense, it presents a clear advantage over Ti-MCM-41 catalysts that are not able to work properly and are not stable when H_2O_2 is used as the oxidant.[29]

As an additional test, we have considered the epoxidation of norbornene on the Ti-containing catalysts. This larger reactant molecule, though it has access to the pores of Ti-Beta, should present stronger restrictions to diffusion than with TiITQ-6. If this is so, TiITQ-6 should give a higher activity than Ti-Beta for the epoxidation of norbornene. The results from Table 5 show that indeed the ratio of activity for norbornene epoxidation on TiITQ-6 and Ti-Beta from the turnover number (TON) at 5 h reaction time is 2.2, while in the case of 1-hexene epoxidation the same ratio was 1.1. It appears then, that while TiITQ-6 shows an intrinsic epoxidation activity similar to that of Ti-Beta using H_2O_2 as oxidating agent, the former presents a benefit when reacting bulky molecules owing to high accessibility of the active sites in the delaminated zeolite.

Conclusions

A new zeolitic material, ITQ-6, has been obtained. This has been produced by delamination of a layered precursor of ferrierite. This material is of zeolitic nature as demonstrated by the different characterization techniques, and consequently is stable upon calcination and presents acid sites of zeolitic nature. It presents a very high external surface area and reactant

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accessibility and, consequently, is able to convert bulky molecules much better than the ferrierite counterpart.

Titanium has been introduced for the first time in the framework of the ferrierite precursor to give Ti−ferrierite and TiITQ-6 by direct synthesis. TiITQ-6 is an active and selective catalyst for the epoxidation of 1-hexene with H_2O_2. The benefit of site accessibility by delamination has been shown catalytically. Moreover, the sample is stable and remains active after repeated reaction−calcination cycles.

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