AlITQ-6 and TiITQ-6: Synthesis, Characterization, and Catalytic Activity**

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The catalytic processes involving ever-larger molecules in the fields of oil refining and the production of fine chemicals have pushed the development of catalytic zeolites towards structures with larger pore diameters.[1–3] The MS-14 molecular sieves, of which MCM-41 is an example, can be used for some catalytic applications with bulky reactants.[4] However, these materials do not show short range order and, from this point of view, are more similar to amorphous than zeolitic materials.

Recently, a new approach for to use zeolites to catalyze the reactions of larger molecules has been undertaken.[5] This approach involves preparation of lamellar zeolites, whose structure is subsequently delaminated, to make accessible all the potentially catalytically active sites.[6] The main difference between this type of material and the mesoporous MCM-41 type materials is that the delaminated zeolites have a short range order and the active sites are, as a consequence, of a 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 larger molecules.[5–7] Unfortunately, although the external surface area of ITQ-2 was above 700 $m^2 g^{-1}$, not all acid sites were accessible from this surface since a system of ten-membered ring (10MR) sinusoidal pores remained. Furthermore, the introduction of transition metals by direct synthesis was unsuccessful and redox catalysts were produced only by anchoring titanium on the external silanol groups through a secondary synthesis.[8] The resultant material was active and selective towards the epoxidation of olefin with organic peroxides but not when the more desirable oxidant H_2O_2 was used.

We have now developed a delaminated zeolite (ITQ-6) as a silicoaluminate (AlITQ-6) and as a silicotitanate (TiITQ-6). The acid and redox-active sites were introduced by direct synthesis and are accessible from the external surface. Herein, we present the synthesis, characterization, and catalytic activity of ITQ-6 systems towards acid and epoxidation reactions using H_2O_2 as oxidant. All results referring to ITQ-6 are as the aluminate form AlITQ-6 unless otherwise specified.

The X-ray diffraction (XRD) patterns of ferrierite (FER)[9] (Figure 1 d) and ITQ-6[10] (Figure 1 c) show, on comparison, that the intensity of the reflections corresponding to planes (0*kl*) are basically indentical, whereas reflections corresponding to planes (*h*00) are strongly diminished in ITQ-6, indicating a remarkable loss of order along the *a* axis. If true, it indicates a delaminated structure and the resultant ITQ-6 material consists mostly of monolayers of the laminar precursor PreFER, as illustrated in Scheme 1. Calcination of PreFER yields FER, whereas the swollen material can be pillared to give ITQ-36[11] or delaminated to produce ITQ-6. In agreement with the delaminated structure, no 10MR pores

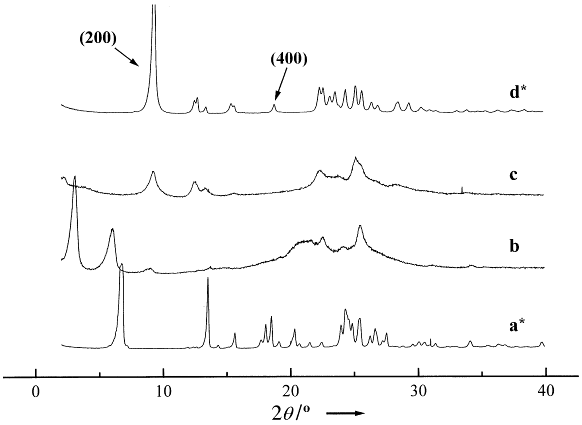
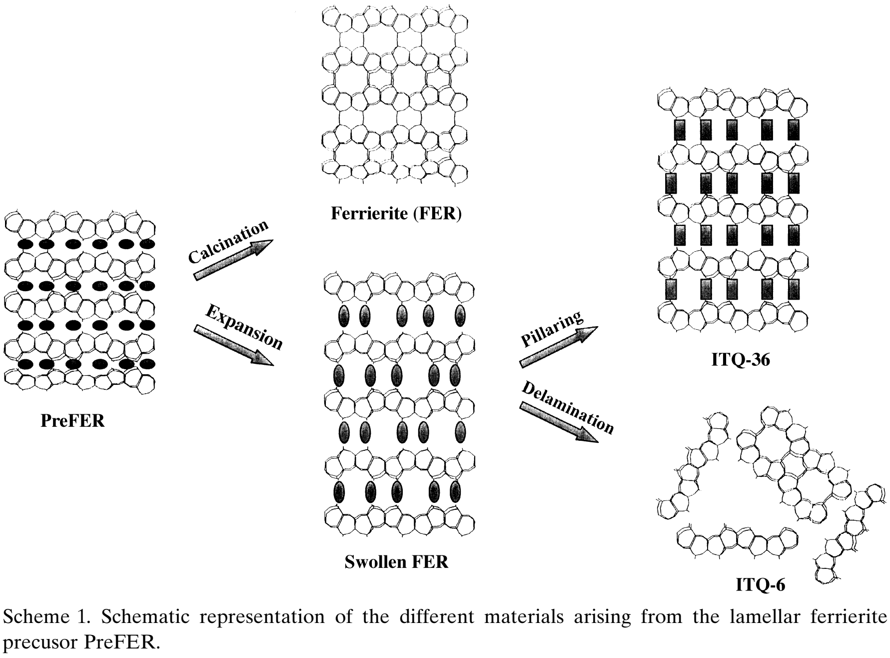


Figure 1. XRD patterns of: a) PreFER, the laminar precursor of ferrierite; b) PreITQ-6, the expanded material; c) ITQ-6, a delaminated zeolite; d) FER, a ferrierite zeolite obtained after calcination of PreFER at 853 K. Spectra marked * are reduced by a third for comparitive purposes.



Scheme 1. Schematic representation of the different materials arising from the lamellar ferrierite precusor PreFER.

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are detected in ITQ-6, as measured by argon adsorption. From nitrogen adsorption isotherms, the external surface areas were calculated for ITQ-6 and FER. The results (Table 1) show that the external surface area ($S_{ext} = S_{tot} - S_{micro}$) has increased by a factor of about 10 after delamination.

Table 1. Specific surface areas (S [m^{2}g^{-1}]) determined from nitrogen adsorption isotherms.

Sample	S_{total} (BET)	S_{micro} (t-plot)
FER	270	210
ITQ-6	618	< 10

It is evident from Scheme 1 that the ITQ-6 material should present a high ratio of Q_3/Q_4 type silicon atoms in where the Q_3 atoms would mainly correspond to terminal SiOH groups oriented towards the external surface of the monolayer. This is indeed seen in Figure 2, in which the ^{29}Si MAS NMR spectra of ITQ-6 and FER are compared. The formation of Q_3 and Q_2 geminal silicon atoms during delamination is also consistent with the large amount of silanol groups detected by IR spectroscopy in ITQ-6 (at 3740 and ca. 960 cm^{-1}; spectra not shown).

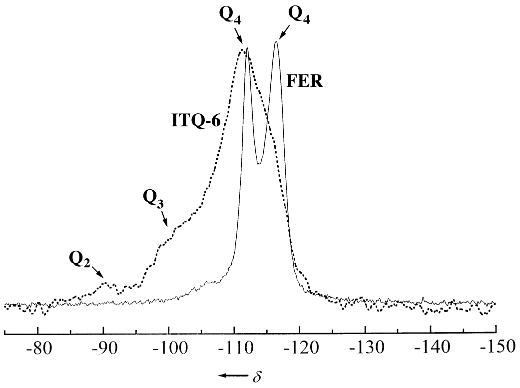

Figure 2. ^{29}Si MAS NMR spectra of FER (calcined PreFER) and ITQ-6 (delaminated PreFER).

It is important to note that the structure of ITQ-6 is stable after calcination at 823 K and a significant amount of the aluminum is still present in the tetrahedral zeolite framework positions, as demonstrated by ^{27}Al MAS NMR spectroscopy (spectra not shown). These aluminum atoms generate strongly acidic sites, as shown by the adsorption–desorption of pyridine (Py) (Table 2). During the delamination process some dealumination has also occurred resulting in a lower concentration of Brønsted acid sites in ITQ-6 (Table 2). However, although the total number of acid sites is somewhat lower for ITQ-6, they become more accessible to bulky molecules than in FER. This feature is demonstrated by measuring the adsorption of 2,6-bis(1,1-dimethylethyl)pyridine (DTBPy, Table 2), which cannot penetrate into the 10MR pores of FER[12].

Differences in the total acidity and the number of accessible Brønsted-acid sites should be reflected in the catalytic activity for cracking *n*-decane and 1,3,5-tris(isopropyl)benzene (TIPB). The comparatively higher activity of ITQ-6 for cracking the sterically bulky TIPB (Table 3) confirms that, through delamination, we have generated a new zeolitic material in which the acid sites in the structure are accessible to larger molecules owing to its very high external surface area. It would be of interest to expand the possibilities of this material by introducing, through direct synthesis, other framework catalytic functions.

Table 3. Catalytic activity[a] (rate of hydrocarbon cracking) of ITQ-6 and FER.

Sample	k [$\times 10^2$ s^{-1}]	
	n-decane	TIPB
FER	0.25	3.5
ITQ-6	0.21	14.0

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

Thus far, the only titanium-rich zeolites prepared by direct synthesis and which show good catalytic performance for oxidation reactions are TS-1, TS-2, and Ti-Beta.[13–15] Although Ti-ZSM-48 was also prepared, it showed no catalytic activity due to pore size constraints.[16] Recently,[17] it has been proposed that the presence of titanium(IV) ions impedes or lowers the nucleation rates in the organothermal synthesis of a titanium-ferrierite system but it was possible to prepare a titanium-containing analogue by seeding with a silicon ferrierite. Unfortunately, the sample had no detectable catalytic activity.[17] In our case, we succeeded in synthesizing directly, without adding seeds, the laminar Ti-PreFER,[11] following the same procedure used for Al-PreFER. The UV/Vis spectrum of the sample shows a single absorption band centered at $\lambda \sim 210$ nm corresponding to an isolated framework of tetrahedrally coordinated titanium atoms. This band remained after calcination (TiFER) as well as after delamination and calcination (TiITQ-6). However, as with AlITQ-6, we observed a degree of titanium extraction from TiITQ-6 during delamination. Nevertheless, we have prepared samples of TiFER and TiITQ-6 with a similar titanium content (1.3 and 1.0 wt %, respectively). The samples were used as catalysts for the epoxidation of 1-hexene with H_2O_2

Table 2. Surface acidity measurements determined by the adsorption–desorption of Py and DTBPy as quantified[a] by IR spectroscopy.

Sample	Total acidity [μmol g^{-1} of Py]						Surface-accessible acid sites (DTBPy adsorption)	
	523 K		623 K		673 K		intensity (3365 cm^{-1})	accessibility [%]
	Lewis	Brønsted	Lewis	Brønsted	Lewis	Brønsted		
FER	2.7	19.3	2.7	16.9	1.4	5.6	< 0.05	< 5
ITQ-6	8.5	9.0	6.4	6.0	5.6	5.4	1.6	90

[a] The integrated molar extinction coefficients of adsorbed pyridine are taken from Emeis.[18]

and the results (Table 4) show that TiITQ-6 is an active and selective olefin epoxidation catalyst with H_2O_2 as an oxidizing agent. Moreover, its activity is much higher than that of TiFER, owing to the higher accessibility of titanium sites, and very similar to the activity of Ti-Beta.

Table 4. Catalytic activity[a] of titanium-containing zeolites for the epoxidation of 1-hexene with hydrogen peroxide.

Sample	X_{hexene}[b] [%]	Selectivity [%][c] to epoxide	of the 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

[a] Reaction conditions are: 16.5 mmol of olefin, 11.8 g acetonitrile, 4.5 mmol H_2O_2, 300 mg catalyst, 323 K, 5 hours. [b] Consumption of 1-hexene relative to the maximum possible. [c] Selectivity values scaled against the maximum possible.

In conclusion, a new zeolitic material, ITQ-6, has been prepared by delamination of a layered precursor of ferrierite. This zeolitic material is stable upon calcination and zeolitic acid sites can be generated. It presents a very high external surface area for reactant accessibility. A novel introduction of titanium into the framework of the ferrierite precursor gives titanium ferrierite and, by direct synthesis, the active and selective epoxidation catalyst TiITQ-6.

Experimental Section

ITQ-6: Silica (10 g, Aerosil 200, Degussa), alumina (2.3 g, as boehmite, Catapal B), NH_4F (9.2 g, Aldrich, 98 %), HF (3.1 g, Aldrich, 49.8 %), (*R*)-4-amino-2,2,6,6-tetramethylpiperidine (26 g, Fluka, 98 % purity), and Milli-Q water (27.9 g) were mixed in an autoclave and left at 448 K for five days. The resulting product (PreFER,[9] Si:Al = 30:1) was filtered, washed with water, and dried at 333 K (XRD in Figure 1 a). The PreFER was expanded to PreITQ-6 through a 16 hours reflux at 368 K as a suspension in an aqueous cetyltrimethylammonium bromide/tetrapropylammonium hydroxide ($CTMA^+Br^-/TPA^+OH^-$) solution (XRD in Figure 1 b). Delamination was performed by placing the PreITQ-6 slurry in an ultrasound bath (50 W, 40 kHz) for one hour, maintaining a pH of 12.5 and a temperature of 323 K. The solid phase was washed thoroughly with water, dried at 373 K (Si:Al = 30:1), and calcined at 853 K for 7 hours yielding ITQ-6 (Si:Al > 40:1; XRD in Figure 1 c). A portion of PreFER was calcined at 853 K without previous treatment to yield FER (XRD in Figure 1 d).

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[1] A. Corma, *Chem. Rev.* **1995**, *95*, 559 – 614.
[2] P. Wagner, M. Yoshikawa, M. Lovallo, K. Tsuji, M. Tasptsis, M. E. Davis, *Chem. Commun.* **1997**, 2179 – 2170.
[3] K. J. Balkus, Jr., A. G. Gabrielov, N. Sandler, *Mater. Res. Soc. Symp. Proc.* **1995**, *368*, 359.
[4] A. Corma, *Chem. Rev.* **1997**, *97*, 2373 – 2419.
[5] A. Corma, V. Fornés, S. B. Pergher, T. L. M. Maesen, J. G. Buglass, *Nature* **1998**, *396*, 353 – 356.
[6] A. Corma, V. Fornés, J. Martinez-Triguero, S. B. Pergher, *J. Catal.* **1999**, *186*, 57 – 63.
[7] A. Corma, U. Diaz, M. E. Domine, V. Fornés, J. L. Jordá, F. Rey, ES-B 9802567, **1999**.
[8] A. Corma, U. Diaz, V. Fornés, J. L. Jordá, M. Domine, F. Rey, *Chem. Commun.* **1999**, 779 – 780.
[9] a) L. Schreyeck, P. H. Caullet, J. C. Mongenel, J. L. Guth, B. Marler, *Chem. Commun.* **1995**, 2187 – 2188; b) L. Schreyeck, P. H. Caullet, J. C. Mongenel, J. L. Guth, B. Marler, *Microporous Mater.* **1996**, *6*, 259 – 271.
[10] A. Chica, A. Corma, U. Díaz, V. Fornés, ES-B 9801689, **1999** and WO 0007722, **2000**.
[11] A. Corma, V. Fornés, A. Chica, U. Diaz, ES-B 9802283, **1999**.
[12] A. Corma, V. Fornés, L. Forni, F. Márquez, J. Martínez-Triguero, D. Moscotti, *J. Catal.* **1998**, *179*, 451 – 458.
[13] M. Taramaso, G. Perego, B. Notari, US-A 4410501, **1983** [*Chem. Abstr.* **1981**, *95*, 206272k].
[14] J. S. Reddy, K. Kumar, O. Ratnasamy, *Appl. Catal.* **1990**, *58*, L1.
[15] A. Corma, P. Esteve, A. Martínez, *J. Catal.* **1996**, *161*, 11 – 19.
[16] D. P. Serrano, H. X. Li, M. E. Davis, *J. Chem. Soc. Chem. Commun.* **1992**, 745 – 746.
[17] R. K. Ahedi, A. N. Kotasthane, *J. Mater. Chem.* **1998**, *8*, 1685 – 1686.
[18] C. A. Emeis, *J. Catal.* **1993**, *141*, 347 – 354.

Ligand-Directed Structural Modification of Imidotin(II) Cubanes: The Mixed Oxidation State Double-Cubanes $[Sn_7\{2\text{-}NR\}_8] \cdot n\,THF$ (R = Pyrimidinyl, 5-Methylpyridinyl)**

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In memory of Ron Snaith

Imidotin(II) cubanes of general formula $[\{SnNR\}_4]$ are the prototypical imidotin(II) compounds. Previous studies have shown that these species are accessible using a variety of synthetic strategies. In certain cases nucleophilic substitution of $SnCl_2$[1] or $SnCp_2$[2] ($Cp = \eta^5\text{-}C_5H_5$) with RN^{2-} or RNH^- can be employed. However, acid–base reactions of the Sn^{II} reagents $[\{Me_2Si(NMe)_2\}Sn]$,[3] $[Sn\{N(SiMe_3)_2\}_2]$,[4] and $[Sn(NMe_2)_2]$[5] with primary amines (RNH_2), hydrazines (H_2NNR), and borylamines (R_2BNH_2) provide more general approaches to these species. Of particular interest to us has been reactions involving $[Sn(NMe_2)_2]$ which have the advantages that they give clean formation of the cubanes for a broad range of amines at low temperatures.[5] The isolation of intermediates of the type $[\{Sn(NR)_2\}(SnNMe_2)_2]$ from the

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