

Ti-ferrierite and TiITQ-6: synthesis and catalytic activity for the epoxidation of olefins with H₂O₂

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A new zeolitic material TiITQ-6 has been obtained by the direct synthesis of a layered titanosilicate precursor, followed by delamination; titanium is tetrahedrally coordinated in framework positions and, while the zeolite derived from the precursor has little activity owing to geometrical constraints, the delaminated TiITQ-6 material is active and selective for the epoxidation of hex-1-ene with H₂O₂.

A new generation of oxidation catalysts started when TS-1¹ was synthesized and showed excellent catalytic activity in aqueous media using H₂O₂ as oxidant. Since then other Ti containing molecular sieves have been synthesized but only a few of them, of which TS-2² and Ti-beta³ are outstanding, have shown to be active and selective for the epoxidation of linear olefins with H₂O₂. Recently⁴ it has been proposed that the presence of Ti⁴⁺ ions tends to impede or to decrease the nucleation rates in the organothermal Ti-ferrierite (TiFER) system but by seeding with Si-ferrierite it was possible to prepare a Ti containing ferrierite. Unfortunately no catalytic activity for the sample was detected.⁴ It was also demonstrated that it was possible to synthesize a laminar aluminosilicate precursor of ferrierite (PREFER)⁵ that upon calcination could produce the ferrierite structure. In our case, we have succeeded in synthesizing directly, without seeding, the titanium containing laminar analogue TiPREFER. This was prepared in the following manner: 10 g silica (Aerosil 200, Degussa), 0.759 g of titanium(IV) ethoxide (Alfa 98%), 28.186 g H₂O (MiliQ), 26.008 g of 4-amino-2,2,6,6-tetramethylpiperidine (Fluka 98%), 9.246 g NH₄F (Aldrich 98%) and 3.462 g HF (Aldrich, 48.1 wt%) were mixed in an autoclave at 408 K for 10 days. The resulting product TiPREFER was filtered off, washed three times, and dried at 333 K. The X-ray diffraction (XRD) pattern of the product is shown in Fig. 1(a). The UV spectrum of the sample shows a single absorption band at ca. 210 nm corresponding to isolated framework Ti in tetrahedral coordination [Fig. 2(a)] and this band was maintained after calcination at 923 K for 12 h [Fig. 2(b)] to produce

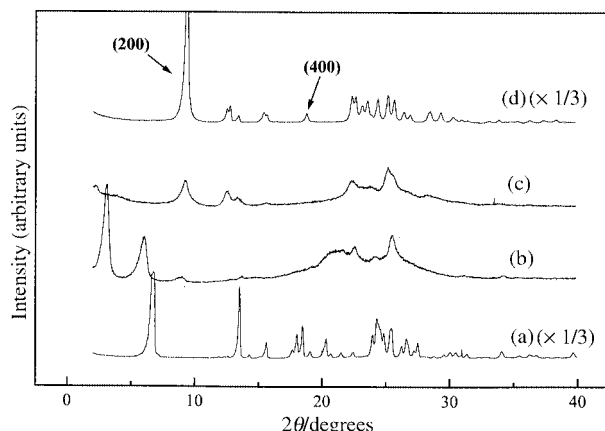


Fig. 1 X-Ray diffraction patterns of (a) TiPREFER, the laminar precursor of Ti-ferrierite, (b) TiPREITQ-6, the expanded material, (c) TiITQ-6, the delaminated zeolite and (d) TiFER, a Ti-ferrierite zeolite obtained after calcination of TiPREFER.

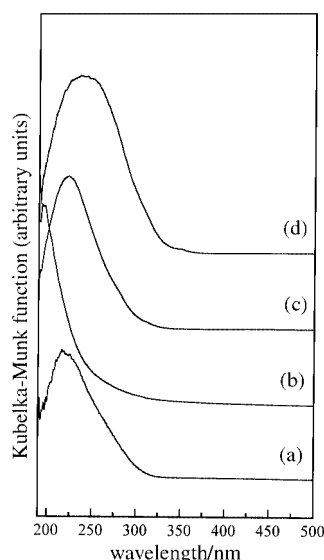


Fig. 2 Diffuse UV-VIS reflectance spectra of TiITQ-6: (a) as synthesized (TiPREFER), (b) Ti-Ferrierite, (c) TiITQ-6 and (d) TiITQ-6 after two reaction-calcination cycles.

the well crystallised Ti containing ferrierite TiFER [Fig. 1(d)]. The catalytic activity of this material for the epoxidation of hex-1-ene with H₂O₂ was tested in a batch reactor in the following way: 16.5 mmol olefin, 11.8 acetonitrile and 300 mg TiFER (1.3 wt% TiO₂) were introduced in a three necked glass flask which was heated to 323 K in a temperature controlled silicon bath. 4.5 mmol H₂O₂ (30% vol) was then added dropwise and the catalytic results obtained are given in Table 1. Very little conversion of hex-1-ene was observed for TiFER owing to diffusion limitation in the pores of this structure, in a similar manner found to that for another unidirectional 10-member ring pore zeolite Ti-ZSM-48.⁶

Table 1 Catalytic activity of Ti zeolites for hex-1-ene epoxidation^a

Sample	X _{hex-1-ene} (% of maximum)	Selectivity to epoxide (%)	Selectivity to H ₂ O ₂ (%)	TON
TiFER	3.2	85.2	23	6
Ti-beta	18.0	97.2	77	20
TiITQ-6	19.7	95.5	73	23
TiITQ-6 ^b	17.7	93.2	56	21

^a Reaction conditions: 16.5 mmol olefin; 11.8 g acetonitrile; 4.5 mmol H₂O₂; 300 mg catalyst; 323 K, 5 h. ^b After two regeneration cycles.

Recently,⁷ a new approach has been undertaken for expanding the use of zeolites to catalyze reactions when the accessibility of the reactants to the active sites is hindered. This involves the preparation of lamellar precursors of zeolites whose structure is subsequently delaminated making potentially catalytically active sites accessible through the external surface. 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.⁸ Unfortunately, the titanosilicate counterpart of ITQ-2 was not synthesized, and oxidation catalysts based on this material could only be prepared *via* secondary synthesis by anchoring Ti on external silanol groups.⁹ The resultant materials were active and selective for epoxidation of olefins with organic peroxides, but they were not active when using the more desirable H₂O₂ as oxidating agent.

Here, we have succeeded in delaminating the Ti laminar precursor of TiFER in the following way: TiPREFER was suspended in a aqueous solution of cetyltrimethylammonium bromide (CTMA⁺Br⁻; 29 wt%) and tetrapropylammonium hydroxide (TPA⁺OH, 40 wt%) and refluxed for 16 h at 368 K. The XRD pattern of the expanded material is shown in Fig. 1(b). Delamination was performed by placing the slurry in an ultrasound bath (50 W, 40 kHz) at 323 K for 1 h, and maintaining the pH at 12.5. Finally the solid phase was washed thoroughly with water, dried at 333 K and calcined at 853 K for 7 h yielding TiITQ-6 with the XRD pattern shown in Fig. 1(c). The Ti in TiITQ-6 remained in tetrahedral coordination as shown by its UV spectrum [Fig. 2(c)]. Some removal of Ti has occurred during the delamination process (*ca.* 25%), nevertheless, when a sample of TiITQ-6 with a similar amount of Ti (1 wt% TiO₂) as in TiFER was prepared it showed a much higher activity and better selectivity for epoxidation of hex-1-ene than TiFER itself (Table 1). The increase in activity of TiITQ-6 is due to the higher accessibility of Ti-sites as a consequence of delamination of the TiPREFER structure. The external surface area of TiITQ-6 is 610 m² g⁻¹ while that of the TiFER is only 60 m² g⁻¹. In addition, the micropore volume of TiFER is 0.1304 cm³ g⁻¹, *cf.* 0.0016 cm³ g⁻¹ for TiITQ-6. From these results it is clear that practically full delamination of the TiPREFER structure has occurred.

In order to have a reference for the catalytic activity of TiITQ-6, we carried out the same under the same conditions using Ti-beta with a similar Ti content (1.3 wt% Ti). The results

in Table 1 show that the activity of TiITQ-6 is similar to that of Ti-beta. Moreover, the stability of TiITQ-6 under the reaction conditions is high since its activity remains close to that of the fresh catalyst after being subject to two reaction-regeneration cycles (calcination at 853 K for 7 h) (Table 1).

In conclusion, TiFER and a new zeolitic titanosilicate material (TiITQ-6) have been synthesized and, while the former presents a low catalytic activity for epoxidation of hex-1-ene with H₂O₂ owing to diffusional limitations of the reactants and products through the unidirectional 10MR channel of the zeolite, TiITQ-6 shows activities and selectivities similar to those of Ti-beta, owing to the good accesibility of the reactants to the active sites achieved by delamination of the TiPREFER laminar precursor.

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Notes and references

- 1 M. Taramaso, G. Perego and B. Notari, *US Pat.*, 4 410 501, 1983.
- 2 J. S. Reddy, K. Kumar and O. Ratnasamy, *Appl. Catal.*, 1990, **58**, L1.
- 3 A. Corma, P. Esteve and A. Martínez, *J. Catal.*, 1996, **161**, 11.
- 4 R. K. Ahedi and A. N. Kotasthane, *J. Mater. Chem.*, 1998, **8**, 1685.
- 5 L. Schreyeck, P. H. Caultet, J. Ch. Mongenel, J. L. Guth and B. Marler, *Chem. Commun.*, 1995, 2187; *Microporous Mater.*, 1996, **6**, 259.
- 6 D. P. Serrano, H. X. Li and M. E. Davis, *J. Chem. Soc., Chem. Commun.*, 1992, 745.
- 7 A. Corma, V. Fornés, S. B. Pergher, Th. L. M. Maesen and J. G. Buglass, *Nature*, 1998, **396**, 353.
- 8 A. Corma, V. Fornés, J. Martínez-Triguero and S. B. Pergher, *J. Catal.*, 1999, **186**, 57.
- 9 A. Corma, U. Diaz, V. Fornés, J. L. Jordá, M. Domine and F. Rey, *Chem. Commun.*, 1999, 779.

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