

Synthesis of an Ultralarge Pore Titanium Silicate Isomorphous to MCM-41 and its Application as a Catalyst for Selective Oxidation of Hydrocarbons

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An ultralarge pore titanium silicate with MCM-41 structure has been prepared by direct hydrothermal synthesis; this material gives rise to useful catalysts for the selective oxidation of small and large organic compounds.

The isomorphous substitution of Si by Ti during the synthesis of zeolites with MFI and MEL structures has generated a new family of titanium containing zeolites named as TS-1 and TS-2, respectively.^{1,2} These zeolites are able to perform the selective oxidation of organic compounds such as alkanes, alkenes and alcohols by H₂O.³⁻⁵ These zeolites, while being active and selective at moderate temperatures, are limited catalytically to molecules which can diffuse into the *ca.* 5.5 Å pore size of their channels. Thus, their activity strongly diminishes when going from n-alkanes to cycloalkanes and branched alkanes.⁶

The possibilities of Ti-zeolites as oxidation catalysts have been enlarged when a Ti zeolite isomorphous with zeolite β was synthesized and shown to be active for the oxidation of cycloalkanes and cycloalkenes.⁷⁻⁹ Nevertheless, the possibilities of Ti-β as oxidation catalyst are limited to molecules with kinetic diameter smaller than *ca.* 6.5 Å. There is no doubt that it exist a strong incentive to synthesize Ti-zeolites with larger pores which can deal with molecules bigger than 6.5 Å, and therefore to become useful oxidation catalysts specially in the field of fine chemicals.

We report here a new Ti-zeolite with pores of 20 Å, and isomorphous with MCM-41 zeolite,¹⁰ which has been obtained by direct synthesis. This ultralarge pore Ti-zeolite is able to carry out the oxidation of hydrocarbons under mild conditions.

Synthesis mixtures were prepared using amorphous silica (Aerosil 200, Degussa), 25% aqueous solution tetramethyl ammonium hydroxide (Aldrich), containing less than 1 and 3 ppm of K⁺ and Na⁺, respectively, and an aqueous solution of hydroxide and bromide of hexadecyltrimethylammonium (Merck). The source of Ti was (C₂H₅O)₄Ti (Alfa). Gels with the following molar chemical composition were prepared: Si:Ti = 60; (CTMA)₂O:TMA₂O = 0.67; (TMA)₂O:SiO₂ = 0.13; H₂O:(TMA)₂O = 188.

The synthesis procedure was as follows: An aqueous solution of tetramethyl ammonium silicate (25% TMAOH, 10% SiO₂), was added to an aqueous solution containing 11.6% and 17.3 wt% of hydroxide and bromide of hexadecyltrimethylammonium, respectively. When the solution was

perfectly homogenized, the SiO₂ and the (C₂H₅O)₄Ti were added.

The resultant gels were heated at 140 °C in an autoclave for 28 h under static conditions. The yield of zeolite was 20%. After filtering, the solid was washed, dried and calcined at 813 K for 1 h in a flow of N₂, followed by 6 h in air.

The powder X-ray diffraction (XRD) (Phillips, Cu-Kα radiation) of the resultant zeolite is presented in Fig. 1 (d-spacing: 28 ± 2 Å), and it corresponds to that reported for the MCM-41 zeolite.¹⁰ The BET (Brunauer-Emmett-Teller) surface area of the sample is 936 m² g⁻¹ the pore volume being 0.49 cm³ g⁻¹. The average pore size of the sample is 20 Å and the Ti content 2.3 wt%, expressed as TiO₂. The sample showed a band at about 960 cm⁻¹ in the IR spectra (KBr pellet technique) (Fig. 2). After impregnation with H₂O₂ this band disappears and the zeolite becomes yellow, the initial condi-

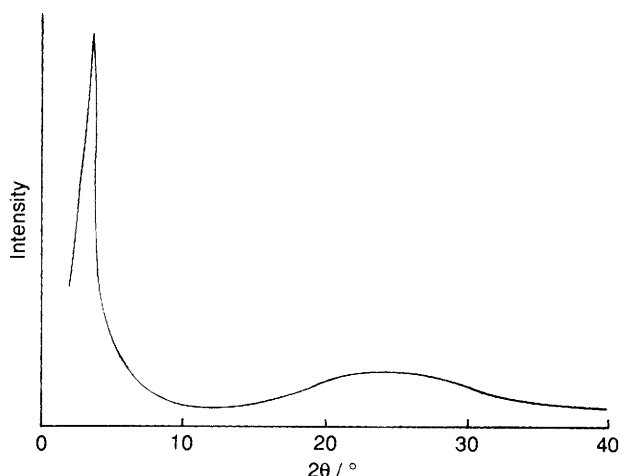


Fig. 1 Powder XRD of the Ti-MCM-41

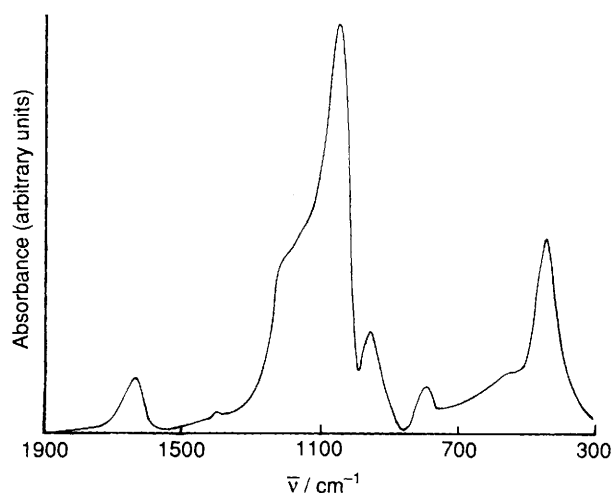


Fig. 2 IR spectra of calcined Ti-MCM-41

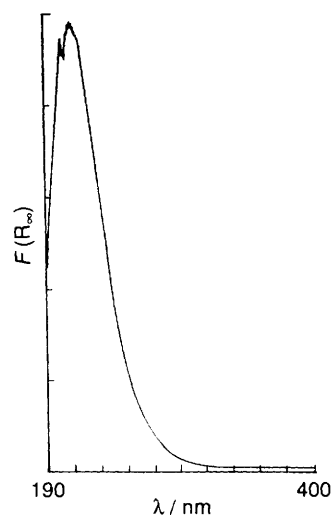


Fig. 3 DR-UV spectra of calcined Ti-MCM-41

Table 1 Catalytic oxidation of hex-1-ene with H₂O₂ on Ti-MCM-41 zeolite

Time/h	Conversion (H ₂ O ₂)	Selectivity (H ₂ O ₂)	Selectivity (% molar)		
			Epoxide	Glycol	Ether
0.50	3.9	60	100	—	—
2.00	23.4	70	95.7	1.7	2.6
3.50	28.9	70	94.4	1.6	4.0
5.00	39.9	75	91.2	3.1	5.7

tions being restored by heating the sample at 353 K overnight. The IR band at 960 cm⁻¹ has been assigned to Ti=O or Si-O-(Ti) group in the zeolite framework^{11,12} and it is usually taken as evidence of the isomorphous substitution Si by Ti.

Fig. 3 shows the diffuse reflectance (DR) spectra in the UV-VIS region of the calcined Ti-MCM-41. It can be seen that there is no peak at ca. 330 nm corresponding to anatase. The sample presented a band at 210–230 nm which has been assigned to isolated Ti atoms in tetrahedral (210 nm) and octahedral (230 nm) coordination.¹³ Thus, considering the characterization results presented, one may conclude that the Ti atoms in Ti-MCM-41 synthesized from alkali-free reaction mixtures occupy framework positions, and have coordination number between 4 and 6.

Concerning the catalytic activity for hydrocarbon oxidation, we present here the epoxidation of hex-1-ene using H₂O₂ (30 wt%, Foret), and norbornene with *tert*-butylhydroperoxide (THP). The reaction with hex-1-ene was carried out in a stirred glass flask. 2.83 g of hex-1-ene were mixed with 23.57 g of methanol, and 0.257 g of the aqueous solution of H₂O₂. 200 mg of the zeolite catalyst were added when the reaction mixture was at 329 K. The advance of the reaction with time, was followed by GC-MS using a 25 m long capillary column with 5% methylphenylsilicone. The results obtained are given in Table 1.

The catalytic behaviour of the Ti-MCM-41 for the oxidation of a larger molecule such as norbornene has been carried out following the same experimental procedure than above, but using a bulky oxidant such as THP. Owing to the size of THP this molecule cannot be used as an oxidant on the TS-1 zeolite. However, when Ti-MCM-41 (100 mg) has been used to oxidize norbornene (1 mmol) with THP in Cl₂CH₂ (THP-

olefin = 12 mol mol⁻¹), at 313 K, 30% conversion was observed after 5 h reaction with 90% selectivity to epoxides, and 10% selectivity to alcohols. The conversion on a Ti-β zeolite⁸ was 20%, while the Ti-ZSM-5 was inactive. Therefore, this new material also opens new possibilities to carry out oxidations in organic synthesis in where organic hydroperoxides are preferred.

In conclusion, an ultralarge pore zeolite with Ti in the framework¹⁴ has been synthesized for the first time. This is able to selectively oxidize olefins and cycloolefins to epoxides at low temperatures. The synthesis of this material, opens the possibility to oxidize bulky molecules of the type involved in the production of fine chemicals.

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