Unseeded synthesis of Al-free Ti-β zeolite in fluoride medium: a hydrophobic selective oxidation catalyst

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Al-free Ti-β zeolite spontaneously nucleates and grows in a reaction mixture containing tetraethylammonium and fluoride ions at near neutral pH, and shows an enhanced crystallinity and thermal and hydrothermal stability as well as a significant hydrophobic character.

Incorporation of Ti in framework positions of zeolites has been shown to produce interesting selective oxidation catalysts. TS-1 (MFI structure, medium-pore zeolite) shows a high activity and selectivity in oxidation reactions using H_2O_2 as oxidant (epoxidation of alkenes, hydroxylation of aromatics, partial oxidation of alkanes, *etc.*).[1] However, due to its medium pore size there are severe steric limitations to the size of both the organic substrate[2] and the oxidating agent.[3] This led us to introduce Ti in other materials with larger pores, such as Ti-β[4] and Ti-MCM-41,[5] for which oxidation of larger organic substrates can be accomplished and larger oxidating agents (such as organic hydroperoxides) can be used.[3] However, the intrinsic activity of those materials seemed to be smaller than that of TS-1 for substrates small enough to show no steric restrictions, at least when methanol was used as the solvent.[6] This was attributed, in the case of Ti-β, to either the presence of Al in the framework, the presence of a high density of connectivity defects (Si–OH groups in the calcined material, giving it extreme hydrophilic properties) or a higher acidity of framework Ti species. While we successfully synthesized Al-free Ti-β by a new method using dealuminated zeolite-β seeds at high pH, the product contained a very high density of Si–OH groups.[7] The resultant catalyst, that we will term here Ti-β(OH), presents a high hydrophilic character (see below) which can be detrimental in selective oxidation reactions, where highly polar compounds (H_2O_2) are combined with organic compounds of less polar character (alkanes, alkenes, aromatics, *etc.*), yielding products of intermediate polarity (alcohols, ketones, epoxides, *etc.*) which can undergo consecutive reactions diminishing the selectivity to the desired product (or even the efficiency in the use of H_2O_2). We have recently developed a new unseeded method for the synthesis of Al-free zeolite-β in fluoride medium,[8] and the zeolite thus obtained is completely free of connectivity defects, which gives this material a strong hydrophobic character. As we report here, the method can be used to produce Al-free Ti-β oxidation catalysts[9] showing some remarkable physicochemical properties that makes them different from previously published Ti-zeolites. The crystallinity of these materials, which we term here Ti-β(F), as well as their thermal and hydrothermal stability are very much improved, while they are essentially hydrophobic in nature.

The synthesis of Al-free Ti-β involves the hydrolysis of tetraethylorthosilicate (Merck) in a water solution containing tetraethylammonium hydroxide (35%, Aldrich, Na < 1 ppm, K < 47 ppm) and H_2O_2, followed by hydrolysis of tetraethylorthotitanate (Alfa) and allowing evaporation of ethanol and water. To the resultant yellow clear solution water lost in the evaporation plus the appropriate amount of HF (48%) were added. The thick yellow paste formed was transferred to 60 ml Teflon stainless-steel autoclaves which are heated at 413 K while being rotated (60 rpm). A typical gel composition corresponds to the formula $TiO_2:60SiO_2:32.9NEt_4OH:32.9HF:20H_2O_2:457.5H_2O$. After 8 days of heating a highly crystalline zeolite-β with 1.2 mass% TiO_2 (in the calcined solid is obtained in a very good yield [23.2 g (100 g of starting mixture)$^{-1}$, amounting to 92.4% incorporation of the inorganic oxides].

The crystallinity of this material is very much improved when compared to a conventional Ti-β(OH) zeolite with the same Ti content. This is true for the as-made materials but it is even more apparent for the calcined ones, where typically a 30% crystallinity is lost for Ti-β(OH) compared to Ti-β(F). Also, the thermal and hydrothermal stabilities are much improved: calcination of Ti-β(F) at 1223 K do not show a lost of crystallinity and Ti remains in the framework, while under the same treatment Ti-β(OH) is completely destroyed. Ti-β(F) is also completely stable to hydrothermal treatments at 1023 K in 100% humidity. We ascribe these effects to the lack of Si–O–Si connectivity defects, which appear in a high concentration in Al-free Ti-β synthesized in OH^- media because of the need to counterbalance NEt_4^+ charges. In the fluoride media, charge balance is achieved with occluded F^-. Other remarkable features of this new generation of Al-free Ti-β materials become apparent when using spectroscopic techniques. First of all, diffuse reflectance ultraviolet (DRUV) spectra show a very narrow charge transfer band centred at *ca.* 210 nm, typical of Ti isolated in a zeolite framework.[10] The width of this band is narrower than the ones presented by conventional Ti-β(OH) and TS-1.

Secondly, X-ray absorption near the Ti K edge spectra (XANES) show an extremely narrow prepeak in the calcined Ti-β(F) sample with only minor changes in intensity after exposure to ambient humidity (Fig. 1). This is in sharp contrast with the results observed with the conventional calcined Ti-β(OH) sample, which show a significant decrease in intensity and a broadening upon rehydration (Fig. 1). We attribute this difference in the prepeak intensities of both types of materials upon rehydration to the strong hydrophobic character of Ti-β(F) (see below and Table 1). Note also that Ti-β(F) samples show a very strong prepeak when compared to other reported Ti zeolites.[11] The prepeak position and intensity (Table 1) are clear indications of stable and uniform tetrahedral Ti species in the calcined dehydrated samples. In the rehydrated samples Ti coordinates water molecules to different extents depending on the hydrophilic [Ti-β(OH)] or hydrophobic [Ti-β(F)] character of the catalysts (Table 1). The peak shift to higher energy with decreasing intensity and increasing width suggest rehydration induces an increase in the coordination number of Ti,[12] giving five- and/or six-coordinate Ti by directly bonding one or two H_2O molecules, this effect being less marked in the Ti-β(F) samples due to their high hydrophobic character.

The remarkable property of Ti-β(F) is its hydrophobic character. While pure SiO_2 zeolite-β prepared by our new procedure[8] is completely hydrophobic and does not adsorb any significant amount of water, incorporation of Ti gives the material a slight but noticeable linear increase in its capacity for water adsorption (*ca.* 2 molecules per framework Ti). However, this capacity is, depending on the Ti content, between 7 and 30 times lower than the water adsorption capacity of Ti-β(OH) catalysts (see Table 1). The high hydrophobic character of Ti-β(F) compared to conventional Ti-β(OH) gives this new catalyst attractive properties in oxidation reactions. As an example, in Table 2 both types of catalysts are compared in the selective epoxidation of esters of unsaturated fatty oils. This reaction is of considerable interest, as epoxides of esterified fatty oils find a wide variety of applications (PVC stabilizers, additives for lubricants, fungicides, algaecides, and in the cosmetic and pharmaceutical industries). As shown in Table 2, Ti-β(F) is more active and selective to the epoxide than Ti-β(OH), and it also uses H_2O_2 much more efficiently. We have also observed an enhanced selectivity to the alcohol in the selective oxidation of alkanes when the hydrophobic Ti-β(F) material is used as a catalyst. We attribute these differences in catalytic performance to the hydrophobic character of Ti-β(F), which minimizes the adsorption of the primary products (the epoxide in the first reaction and the alcohol in the second one), then minimizing consecutive reactions which would diminish the selectivity to the desired product. The paramount importance of the hydrophobic/hydrophilic character of Ti-zeolites in selective oxidation reactions will be fully described elsewhere.

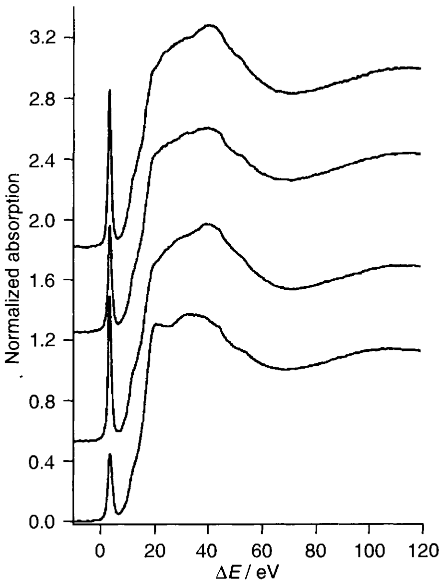

Fig. 1 Ti-K edge XANES spectra of calcined Al-free Ti-β catalysts. From top to bottom: Ti-β(F) dehydrated and rehydrated and Ti-β(OH) dehydrated and rehydrated.

Table 1 Ti K-edge XANES prepeak parameters of calcined Al-free Ti-β(F) and Ti-β(OH)

Catalyst	%TiO_2 (mass)	State	Intensity[a]	Position[b]/ eV	FWHM/ eV	Area
Ti-β(F)	2.18	Dehydrated	1.03	3.80	1.32	1.76
		Rehydrated[c] (2.1)	0.71	3.90	1.46	1.36
Ti-β(OH)	3.35	Dehydrated	0.96	3.81	1.35	1.67
		Rehydrated[c] (36.4)	0.42	4.06	1.86	1.00

[a] Relative to the beginning of the EXAFS oscillations. [b] Relative to the first inflection point for Ti metal (±0.2 eV). [c] Values in parentheses are moles of water readsorbed per unit cell.

Table 2 Activity and selectivity of Al-freeTi-β(F) and Ti-β(OH) in the epoxidation of methyl oleate with H_2O_2[a]

		Conversion (mol%)		Selectivity	
Catalyst	TiO_2 (% m/m)	Methyl oleate	H_2O_2	Epoxide	H_2O_2
Ti-β(F)	2.2	81.2	96.6	95.1	55.7
Ti-β(OH)	3.3	27.6	97.5	80.2	17.8

[a] Reaction conditions: 296.5 mg methyl oleate, 2 ml MeCN, 126.6 mg H_2O_2 (35 mass%), 60 mg catalyst, 60 °C, 15 h.

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