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## Synthesis of Titanium-containing ZSM-48

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Titanium-containing ZSM-48 is synthesized with silicon to titanium ratios of 26 or larger; changes in unit cell volume and IR data show that titanium is incorporated into framework positions.

Titanium silicalite-1 (TS-1)<sup>1</sup> is a remarkable catalytic material capable of promoting the reaction of aqueous hydrogen peroxide with a broad spectrum of organic substrates, *e.g.* alkenes, alkanes or aromatics,<sup>2,3</sup> selectively to yield partial oxidation products. Currently, Enichem produces hydroquinone and catechol by oxidizing phenol over TS-1 with aqueous H<sub>2</sub>O<sub>2</sub>.<sup>2</sup> TS-1 is a medium-pore molecular sieve with the ZSM-5 topology. Although the synthesis of TS-1 is somewhat difficult, several methods can be used (all use tetrapropylammonium hydroxide as a structure-directing agent).<sup>1,4</sup> Recently, TS-2, the titanium-containing pure-silica ZSM-11 molecular sieve, has also been synthesized.<sup>5,6</sup> ZSM-5 and ZSM-11 are structurally very similar. In fact, pure-silica ZSM-5 and ZSM-11 can be synthesized using the same procedure except that tetrabutylammonium hydroxide is substituted for tetrapropylammonium hydroxide when synthesizing ZSM-11. The relationships between the synthesis of TS-2 and TS-1 are analogous to those between ZSM-11 and ZSM-5. Additionally, the catalytic behaviour of TS-2 is similar to that of TS-1 as expected.<sup>6-10</sup>

The physicochemical properties of TS-1 and TS-2 that are deemed necessary for the catalytic applications of these materials include (i) the absence of trivalent ions, *e.g.* Al<sup>3+</sup>, that could lead to the formation of acid sites and (ii) framework incorporation of the titanium atoms. For many of the proposed applications of TS-1 or TS-2, the presence of acidity is detrimental to the ultimate catalyst selectivity.<sup>2</sup> Thus, these materials must be composed of silicon and titanium oxides. Framework titanium has been found to be

critical to the catalytic performance of TS-1 or TS-2 alone. Bellussi and Fattore<sup>11</sup> have reviewed the preparation of titanium-containing zeolites. If substitution of titanium for silicon occurs the unit cell size of the molecular sieve should increase. Also, it has been observed that an IR absorption peak at 960 cm<sup>-1</sup> is indicative of Ti<sup>4+</sup> siting in a silicate framework (TS-1 or TS-2) and that the intensity of the band can be related to the amount of titanium present.<sup>11</sup> Recently, Behrens *et al.*<sup>12</sup> showed from XANES and EXAFS investigations of TS-1 that the titanium is octahedrally coordinated. On the other hand, Lopez *et al.*<sup>13</sup> found from EXAFS analyses that hydrated TS-1 contains octahedrally coordinated titanium and that dehydration transforms the titanium from octahedral to tetrahedral coordination. Both investigations conclude that titanium is incorporated into framework positions.

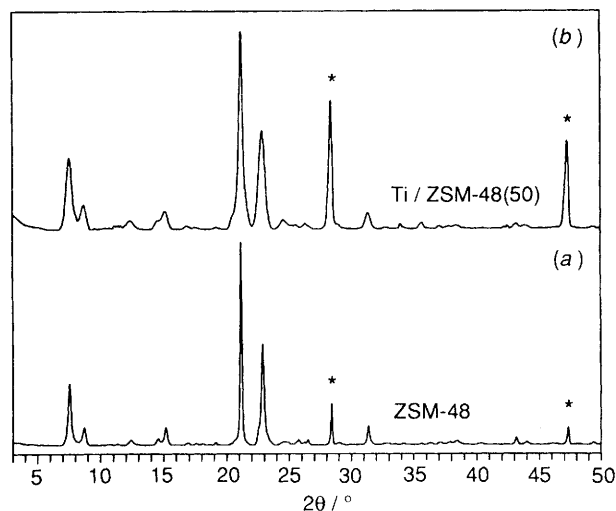
Although TS-1 was synthesized almost a decade ago, Bellussi and Fattore<sup>11</sup> conclude that there is no clear evidence that titanium atoms are inserted into the frameworks of any materials other than ZSM-5 (TS-1) and ZSM-11 (TS-2). Here we report the synthesis and partial characterization of Ti/ZSM-48. (ZSM-48 is a unidimensional, medium-pore, high-silica zeolite.<sup>14</sup>) Ti/ZSM-48 is the first non-ZSM-5 or ZSM-11 pure-silica molecular sieve to be synthesized with titanium incorporated into framework positions.

TS-1 has been synthesized by three different procedures. The first involves the use of silicon and titanium alkoxides, *e.g.* example 1 of ref. 1. The second includes a step for the formation of peroxytitanates by the reaction of aqueous H<sub>2</sub>O<sub>2</sub> with a second aqueous solution containing hydrolysed titan-

**Table 1** Properties of titanium silicate ZSM-48

Sample	Si/Ti in gel	Si/Ti in product <sup>a</sup>	n-Hexane adsorbed <sup>b</sup> (g/g)	Unit cell volume/ <sup>c</sup> Å <sup>3</sup>
ZSM-48	∞	Not measured	0.035	2416
Ti/ZSM-48(100)	100	66.2	0.054	2426
Ti/ZSM-48(50)	50	49.5	0.068	2433
Ti/ZSM-48(30)	30	26.1	0.067	2438

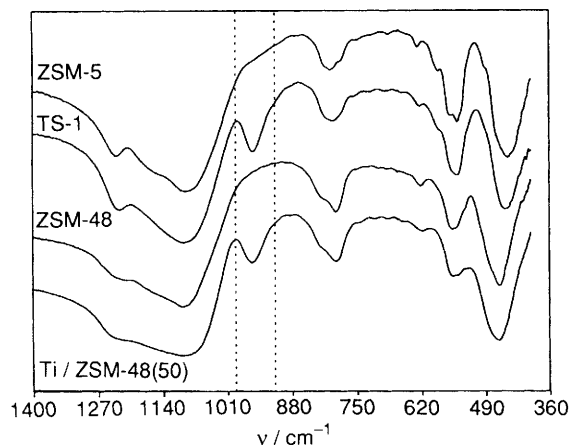
<sup>a</sup> Molar ratio obtained from bulk chemical analysis. <sup>b</sup> Measured with a McBain-Bakr balance; samples were calcined in air at 600 °C (Ti/ZSM-48) and 630 °C (ZSM-48);  $P_{\text{hexane}} = 40$  Torr; ambient temp. <sup>c</sup> Calculated from X-ray powder diffraction data.



**Fig. 1** X-Ray powder diffraction patterns of (a) pure-silica ZSM-48 and (b) Ti/ZSM-48(50). Peaks marked are from silicon internal standard. Data collected on a Scintag XDS 2000 diffractometer equipped with a liquid nitrogen-cooled germanium solid-state detector and using Cu-K $\alpha$  radiation.

ium alkoxides, *e.g.* example 2 of ref. 1. The third method involves the wetness impregnation of a coprecipitated, amorphous TiO<sub>2</sub>-SiO<sub>2</sub> with an aqueous solution of tetrapropylammonium hydroxide.<sup>4</sup> Note that in all cases tetrapropylammonium hydroxide is used as a structure-directing agent. Additionally, it is critical that no alkali cations be present in the synthesis mixtures,<sup>7</sup> even at ppm levels.<sup>11</sup> Alkali cations are most commonly used to synthesize high-silica zeolites. However, ZSM-5 and ZSM-11 are two of the very limited number of structures that do not require alkali cations to be present in the synthesis mixture for their preparation. Thus, extensions from the TS-1 (and TS-2 which is synthesized by either methods 1 or 2 listed above) synthesis procedures to the crystallization of other titanium silicates are not straightforward.

Pure-silica ZSM-48 can be synthesized in the absence of alkali cations.<sup>15</sup> Thus, we started our syntheses of new titanium silicate molecular sieves by synthesizing titanium-containing ZSM-48 (Ti/ZSM-48). A typical procedure is as follows. Titanium tetrabutoxide (0.34 g) was added to doubly distilled, deionized water (9.2 g) whereupon a white precipitate (hydrous titanium oxide) was formed. Aqueous H<sub>2</sub>O<sub>2</sub> (0.63 g; 30 wt% H<sub>2</sub>O<sub>2</sub>) was added to the stirred slurry and stirring continued at room temperature for 2 h. The hydrous titanium oxide dissolved on reaction with H<sub>2</sub>O<sub>2</sub> to form soluble peroxytitanates. A second solution was prepared by adding of Cab-O-Sil (M5) fumed silica (3 g) to H<sub>2</sub>O (31.5 g). Solution 1 was added dropwise to well-stirred solution 2 and upon complete addition blended for an additional 3 h. Finally a solution containing diaminoctane (3.1 g) and water (17.5 g)



**Fig. 2** IR spectra of molecular sieves (Nicolet 800 Fourier-transform instrument)

was added dropwise to the foregoing mixture. The complete reaction mixture was stirred for 1 h, charged into Teflon-lined autoclaves and heated at 175 °C for 10 days. The autoclaves were rotated at 50 rev min<sup>-1</sup>. The product was collected by filtration.

This sample is labelled Ti/ZSM-48(50) (Si/Ti = 50). For Ti/ZSM-48(100) and Ti/ZSM-48(30), only the amount of titanium tetrabutoxide was changed to give Si/Ti = 100 and Si/Ti = 30, respectively. The H<sub>2</sub>O<sub>2</sub> : Ti ratios used in synthesizing TS-1 and Ti/ZSM-48 are approximately 25 : 1 and 5 : 1, respectively. Thus, less H<sub>2</sub>O<sub>2</sub> is employed for synthesizing Ti/ZSM-48. If an H<sub>2</sub>O<sub>2</sub> to Ti ratio of 50 : 1 is used in attempting to synthesize Ti/ZSM-48, only an amorphous solid is obtained. In the preparation of TS-1, the final mixture is heated at 70–80 °C for 6–7 h before heating in the autoclave. This step is not necessary when synthesizing Ti/ZSM-48.

Table 1 shows the physicochemical properties of Ti/ZSM-48 samples and of pure-silica ZSM-48 for comparison. Ti/ZSM-48 can be synthesized from gels containing Si/Ti  $\geq$  30 and the Si/Ti ratio in the product reflects the ratio in the precursor in most cases. For high Si/Ti ratios in the gel, the product tends to concentrate the titanium. TS-1 is typically synthesized for Si/Ti = *ca.* 30. Thus, Ti/ZSM-48 can be synthesized at a bulk composition similar to TS-1. Fig. 1 shows the X-ray powder diffraction patterns of ZSM-48 and Ti/ZSM-48(50); no peaks other than those ascribable to the ZSM-48 framework are observed. Additionally, the peaks for Ti/ZSM-48 are broader than those for ZSM-48, most likely owing to particle size effects and not a loss of crystallinity (see hexane adsorption results in Table 1). The Ti/ZSM-48 crystals are significantly smaller than those of pure-silica ZSM-48. As mentioned above, if titanium is located within the framework, the unit cell size should increase. The complete X-ray powder diffraction patterns of ZSM-48 and Ti/ZSM-48 were indexed and the unit cell dimensions refined using an orthorhombic cell. The unit cell volumes of the samples studied here are listed in Table 1 and increase with decreasing Si/Ti. Additional evidence for framework siting of Ti is given in Fig. 2. TS-1 and Ti/ZSM-48 (all samples) reveal an IR band at around 960 cm<sup>-1</sup> while pure-silica ZSM-5 and ZSM-48 do not. Also, no indication of bulk TiO<sub>2</sub> is observable by Raman spectroscopy. The Raman spectra of TS-1 and Ti/ZSM-48 show only one additional peak, at 960 cm<sup>-1</sup>, in the 1000–400 cm<sup>-1</sup> region compared with the spectra obtained from pure-silica ZSM-5 and ZSM-48. The adsorption of n-hexane was used to test for the presence of intracrystalline amorphous material. The adsorption capacity for n-hexane on the Ti/ZSM-48(50) and Ti/ZSM-48(30) samples is that which is expected from the ZSM-48 structure.<sup>14</sup> Thus, we believe that the titanium in the Ti/ZSM-48 samples is located within the framework. Note that the adsorption capacity of pure-silica ZSM-48 is low, owing to

the presence of residual carbon. Thermogravimetric analysis shows that Ti/ZSM-48 does not contain any mass remaining from the decomposition of the organic structure-directing agent at 600 °C whereas some organic material remains in pure-silica ZSM-48 until 800 °C. Additionally the Ti/ZSM-48 samples are white after calcination at 600 °C and the pure silica ZSM-48 is tan after calcination at 630 °C. Ti/ZSM-48(100) most likely has a small amount of residual carbon as well (from thermogravimetric analysis) that accounts for the slightly lower adsorption capacity when compared to the other Ti/ZSM-48 samples.

Ti/ZSM-48 is the first non-ZSM-5 or ZSM-11 titanium silicate to have titanium incorporated into framework positions. Since the pore structure of ZSM-48 is significantly different from either ZSM-5 or ZSM-11 we expect that Ti/ZSM-48 will reveal shape-selective catalytic behaviour unlike that observed from TS-1 and TS-2. Catalytic testing of Ti/ZSM-48 is in progress.

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