Synthesis of Titanium Silicalite-1 from an SiO_2–TiO_2 Cogel using a Wetness Impregnation Method

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An alternative to the conventional methods of TS-1 synthesis is based on the wetness impregnation of an SiO_2–TiO_2 cogel, which leads to more effective Ti incorporation in a simpler way.

Titanium silicalite-1 (TS-1) is a molecular sieve with the MFI structure and has Ti atoms inserted in the framework.[1] TS-1 has been shown to be a very effective catalyst for oxidation reactions, such as phenol hydroxylation,[2,3] propene epoxidation,[4] cyclohexanone ammoxidation[5] and alkane oxyfunctionalization.[6] The use of H_2O_2 as oxidant under mild reaction conditions (temperature usually below 100 °C) allows high selectivities towards the partial oxidation products to be obtained.

TS-1 was first synthesized 10 years ago.[7] However, the number of research groups now working with this material is still relatively low. Likewise, few of other zeolite structures have been synthesized that contain Ti atoms in framework positions: TS-2 (MEL structure),[8] TiAl/beta[9] and Ti/ZSM-48.[10] The origin of these limitations lies in the difficulty of incorporating the Ti atoms in the zeolite lattice, since they tend to precipitate as TiO_2 during the gel preparation or during the synthesis. The conventional method of preparation of TS-1 has to be carried out very carefully under controlled conditions: the Si and Ti alkoxides are hydrolysed by the addition, dropwise and very slowly, of tetrapropylammonium hydroxide (TPAOH) at 0 °C, under a nitrogen atmosphere and in the complete absence of alkali-metal cations.[11] Even with these precautions, a white precipitate of TiO_2 is often observed in the starting gel.[12]

In this work, we have studied a new and much simpler method of preparation of TS-1. It is based on the procedure initially developed by Padovan *et al.*[13]: SiO_2–TiO_2 coprecipitates, supplied by Grace, are converted into TS-1 by wetness impregnation with a TPAOH solution: the dried coprecipitate is impregnated with a quantity of the template solution similar to the pore volume of the solid. We have modified this method by replacing the coprecipitate by SiO_2–TiO_2 cogels prepared in our laboratory using the sol–gel process, which allows us to control the properties and chemical composition of the raw material. In these cogels, the Ti and Si atoms are bound through oxygen bridges analogous to those present in TS-1, stabilizing the Ti atoms and preventing the TiO_2 precipitation during the synthesis process. The preparation of the cogels is carried out by a two-step (acid–base) sol–gel process: the Si and Ti alkoxides are first hydrolysed in an acid medium (the acid-catalysed hydrolysis is slower than the base-catalysed hydrolysis, which avoids TiO_2 precipitation at this stage) and the liquid is then converted into a solid cogel by addition of a base (ammonia, TPAOH). Finally, TS-1 is obtained by wetness impregnation of the dried cogel with a TPAOH solution and crystallization under autogeneous pressure. A typical procedure of preparation is as follows: tetraethylorthosilicate (TEOS, Aldrich) was hydrolysed at room temperature with 0.05 mol dm^{-3} aqueous HCl. Titanium tetrabutoxide (TNBT, Aldrich), previously dissolved in isopropyl alcohol, was added and the clear liquid obtained was stirred for 15 min. Formation of a solid cogel was caused by the addition of a 20% TPAOH aqueous solution (Alfa). After the cogel had been dried overnight at 110 °C, it was wetness-impregnated with 20% aqueous TPAOH solution (1.6 g of solution per g of cogel) and the mixture was charged into Teflon-lined autoclaves, the crystallization being carried out under static conditions at 170 °C for 24 h. The sample of conventional TS-1 used as the reference was prepared according to the method previously reported in the literature.[14] In both cases, the final product was washed several times with distilled water, dried at 110 °C and calcined at 550 °C for 3 h.

The molar composition, as well as, the time and crystalline yield of both synthesis are summarized in Table 1. Both samples were prepared with an Si : Ti ratio of 30 in the initial mixture, but the proportion of TPAOH necessary to crystallize TS-1 by wetness impregnation is half than that used in the conventional method. Likewise, the volume occupied by the reaction mixture and, therefore, the volume of the synthesis reactor is fourfold higher in the case of the conventional route. Additional advantages of the wetness impregnation method are the high TS-1 yield obtained (practically 100%) and the

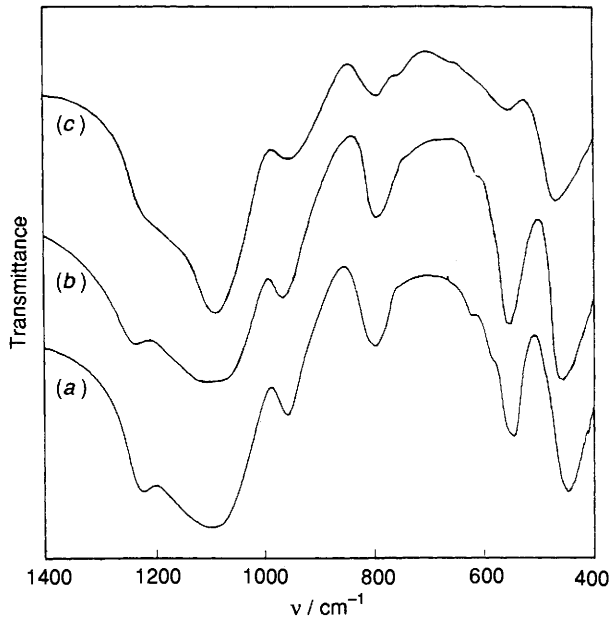

Fig. 1 IR spectra of TS-1 synthesized by (*a*) the conventional method (*b*) wetness impregnation; (*c*) IR spectrum of the SiO_2–TiO_2 cogel

Table 1 Gel composition, synthesis time (t_s) and crystalline yield (Y_c)

	Molar gel composition					
Sample	SiO_2	TiO_2	TPAOH	H_2O	t_s/days	Y_c (%)
TS-1 (conv.)	30	1	9.8	1135	6	86
TS-1 (w.i.)	30	1	4.4	164	1	100

Table 2 Crystallinity (C),[a] unit-celll volume (V_{uc}),[b] I_{960}/I_{800}[c] and average crystal size (d_c)[d]

Sample	C (%)	V_{uc}/Å^3	I_{960}/I_{800}	d_c/μm
TS-1 (conv.)	94	5341	1.5	0.15
TS-1 (w.i.)	100	5361	1.7	2.50

[a] Calculated from the peak areas between $2\theta = 22$–$25°$ in the XRD spectra. [b] Determined from powder XRD data. [c] Ratio between the intensities, in absorbance units, of the IR bands at 960 and 800 cm^{-1}. [d] Measured by SEM.

Table 3 Catalytic properties in *n*-hexane oxidation[a]

Sample	*n*-Hexane conversion (%)	H_2O_2 conversion (%)	H_2O_2 selectivity (%)[b]	Product distribution (mol%) Hexanol-2-ol	Hexan-3-ol	Hexan-2-one	Hexan-3-one
TS-1 (conv.)	22.5	40.0	63.9	21.7	44.3	18.2	15.8
TS-1 (w.i.)	43.7	79.3	62.6	23.4	43.4	20.0	13.2

[a] Reaction conditions: T = 100 °C, t = 1 h. Composition of the reaction mixture: H_2O_2/*n*-hexane mole ratio = 1.176, *n*-hexane/acetone mass ratio = 0.278, *n*-hexane/TS-1 mass ratio = 12.42. [b] Defined as (moles hexanol + 2 × moles hexanone)/moles H_2O_2 converted.

synthesis time. In relation to the latter, a kinetic experiment was carried out, showing that the crystallinity of the sample prepared by wetness impregnation after 6 h of synthesis is *ca.* 84%.

The crystallinity, symmetry and unit-cell volume of both samples were calculated from their powder XRD patterns after they had been calcined (see Table 2). Both materials were highly crystalline with an orthorhombic symmetry instead of the monoclinic structure of silicalite-1, in agreement with the presence of Ti atoms in framework positions. Moreover, the unit-cell volume is clearly higher for both TS-1 samples than the value determined for a sample of silicalite-1 (5286 Å^3), which is usually considered to be a consequence of the incorporation of Ti into the lattice.[15] Therefore, the higher unit-cell volume of the sample prepared by wetness impregnation suggests that Ti is incorporated more effectively by this method.

Further evidence of the Ti insertion in the structure is the presence of a band at 960 cm^{-1} in the IR spectra of TS-1 related to the stretching vibration of SiO_4 units bound to Ti atoms. The relative intensity of this band correlates well with the Ti content of the material.[14] Fig. 1 shows the IR spectra of both TS-1 samples and that corresponding to the SiO_2–TiO_2 cogel used as the raw material. It is remarkable that this band can be clearly observed in the cogel, showing how its preparation by sol–gel methods allows the formation of Si–O–Ti bonds prior to crystallization. As can be seen in Table 2, using as reference the 800 cm^{-1} IR band ascribed to the symmetric stretching of the linkages between SiO_4 tetrahedra in the zeolite framework, the ratio between the intensities of the 960 and 800 cm^{-1} IR bands is higher for TS-1 prepared by wetness impregnation, again suggesting a higher degree of Ti incorporation in this sample.

The major difference between the physicochemical properties of the TS-1 samples is concerned with their crystal size (Table 2). The crystals prepared by the conventional method are smaller than those obtained by wetness impregnation, which could lead to significant differences in their catalytic behaviour in reactions controlled by intracrystalline diffusion. However, if wetness impregnation is carried out with a more concentrated TPAOH solution (30%), the average crystal size obtained is 0.25 μm, showing that the crystal size can be controlled changing the synthesis conditions.

Finally, the catalytic properties of both samples have been compared using the selective oxidation of *n*-hexane as a test reaction.[16] The catalytic experiments were carried out in stirred autoclaves, under autogeneous pressure with H_2O_2 as oxidant and acetone as solvent. The reaction conditions and the results obtained are summarized in Table 3. Both *n*-hexane and H_2O_2 conversions are almost twice as high for the TS-1 sample prepared from the cogel, whereas the efficiency or selectivity in the use of H_2O_2 and the product distribution are similar for both samples. The higher *n*-hexane oxidation activity showed by the TS-1 sample prepared by wetness impregnation is likely to be related to the more effective incorporation of Ti into the framework, as shown by the XRD and IR data.

Wetness impregnation of an SiO_2–TiO_2 solid prepared by the sol–gel processes is a simple method for the synthesis of TS-1 which prevents TiO_2 precipitation, leading to a material with a higher degree of incorporation of Ti than that obtained by the conventional synthesis procedure.

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