An Easy Way to Prepare Titanium Silicalite-1 (TS-1)

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Titanium silicalite-1 (TS-1) is easily synthesized using an aqueous solution of $TiCl_3$ as the titanium source.

Titanium silicalite-1 (TS-1) has attracted much attention during the last decade because of its remarkable catalytic properties in selective oxidation involving H_2O_2 as the oxidant.[1] It is assumed that titanium atoms existing in TS-1 lattice positions, replacing silicon atoms, are the active sites in catalytic reaction.[2] In the original patent,[3] samples were prepared by hydrothermal crystallization of precursor gels containing tetraethyl orthosilicate $Si(OEt)_4$ to supply silicon, tetraethyl titanate $Ti(OEt)_4$ as the titanium source, tetrapropylammonium hydroxide TPAOH solution as the template. The most critical part of the synthesis was to avoid precipitation of TiO_2 in the addition of the organic template. Later, Thangaraj *et al.*[4] reported a second synthetic route in which the more stable $Ti(OBu)_4$ was used as titanium source instead of $Ti(OEt)_4$. Moreover, Bu^tOH was added to slow the hydrolysis of titanium alkoxide.

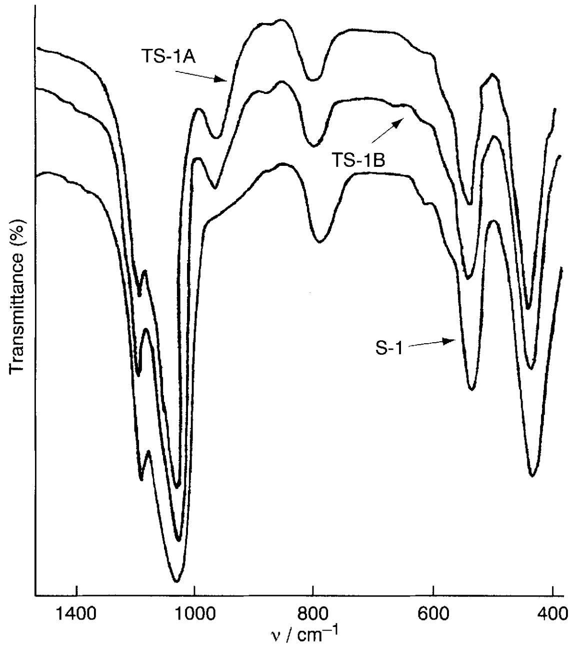

Fig. 1 FT–IR spectra of titanium silicalite-1: TS-1A prepared using an aqueous solution of $TiCl_3$ as the titanium source, TS-1B prepared according to the patent[3] using $Ti(OBu)_4$ as the titanium source. $SiO_2:TiO_2$ molar ratio: TS-1A, 55; TS-1B, 55.9. S-1 is silicate without the Ti activator.

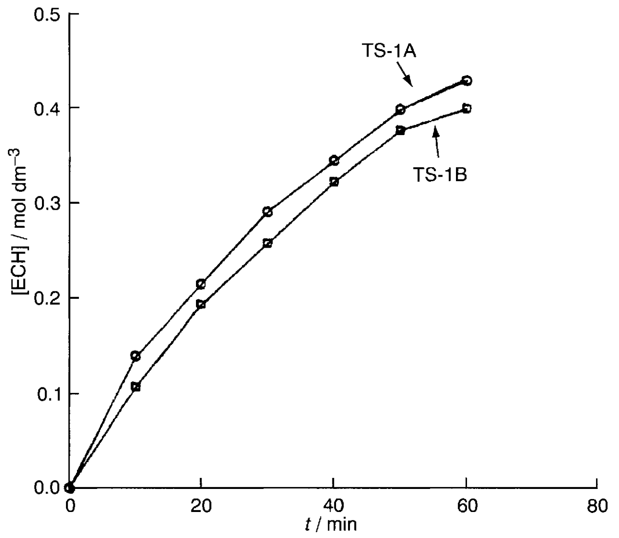

Fig. 2 Epoxidation of allyl chloride catalysed by titanium silicalite-1. (ECH = epichlorohydrin produced). *Reaction conditions*: temperature, 45.0 °C; solvent, methanol; catalyst, 8.00 g l^{-1}; allyl chloride, 1.214 mol dm^{-3}; H_2O_2, 0.517 mol dm^{-3}; magnetic stirring. H_2O_2 conversion after 60 min reaction: TS-1A, 84.4%; TS-1B, 77.6%. H_2O_2 selectivity to product after 60 min reaction: TS-1A, 99.5%; TS-1B, 99.7%.

Here we describe an easy method for the preparation of TS-1: the precipitation of TiO_2 during the preparation of the precursor mixture can be avoided easily by using an aqueous solution of $TiCl_3$ as the titanium source. Moreover, the synthetic procedure is simplified. In a typical synthesis experiment, 70 g of TPAOH (20% aqueous solution, Aldrich) was added to $Si(OEt)_4$ (50 g) solution under magnetic stirring. To the resulting colourless solution, an aqueous solution of $TiCl_3$ was added. After heating to 80–90 °C for *ca.* 3 h, the mixture was transferred into a 120 ml PTFE-lined autoclave to crystallize at 433 K for 2–5 d. The solid was obtained by filtration and was finally calcined at 550 °C for at least 8 h.

The IR spectra (FT–IR, Nicolet 10 DX FT) of the sample (Fig. 1, TS-1A) synthesized from $TiCl_3$ exhibits an adsorption band at 970 cm^{-1} which is characteristic of TS-1 molecular sieves, and is related to the active sites.[5] X-Ray powder diffraction experiments (XRD, D/max-RBX) show the sample to be phase pure and free from anatase. Transmission electron microscopy (TEM, JEM-1200) found that the TS-1A sample consisted of highly crystalline cubes of size 0.15 μm.

The results of catalytic epoxidation of allyl chloride are shown in Fig. 2, where the concentration of the epichlorohydrin produced is plotted against reaction time. Here, the TS-1A sample was prepared by the method described above ($TiCl_3$), and the TS-1B sample was prepared according to the patented method[3] using $Ti(OBu)_4$ as the titanium source. From these results we can conclude that the TS-1A sample has comparable reactivity to that of the sample prepared by the classical method.

In conclusion, highly effective titanium silicalite-1 can be prepared easily using an aqueous solution of $TiCl_3$, and the route of preparation has also been simplified. It should be noted that some other templates (or pore fillers) can be used in the preparation of highly effective TS-1 molecular sieves if an aqueous solution of $TiCl_3$ is used as the titanium source.

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