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A NEW METHOD FOR THE PREPARATION OF TITANIUM-SILICALITE (TS-1)

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Titanium-silicalite can be prepared by subsequent dealumination of ZSM-5 with hydrochloric acid and reaction with titaniumtetrachloride vapour at elevated temperatures. The titanium atoms are probably inserted into lattice vacancies which were formed upon acid leaching.

Titanium-silicalite (TS-1) is a titanium derivative of silicalite-1 (ZSM-5) which is assumed to contain titanium atoms in lattice positions replacing silicon atoms. This new material has promising catalytic properties in the field of oxidation reactions involving hydrogen peroxide [1–4]. The synthesis of TS-1 by hydrothermal reaction of tetraethylorthotitanates, a silicon source, tetrapropylammonium hydroxide and water has first beem claimed by Taramasso et al. [5].

Here, we describe an alternative route for the preparation of TS-1. The starting material is ZSM-5 with a framework Si/Al ratio of 50. The threefold treatment with 1 N HCl solution at 353 K results in a material with Si/Al ratio of about 2000. The reaction with $TiCl_4$ is performed in a vertical quartz glass reactor. Prior to the reaction, the highly siliceous ZSM-5 is dried overnight at 723 K in a stream of purified and dried nitrogen. Then, nitrogen is saturated with $TiCl_4$ at room temperature and passed through the reactor at temperatures between 673 and 773 K. After completion of the reaction the product is purged with nitrogen at 773 K overnight and cooled down.

The results of the X-ray diffraction analyses are shown in Table 1. The unit cell constants have decreased after dealumination of ZSM-5 and have again increased after subsequent reaction with $TiCl_4$. The increase in unit cell constants is more pronounced for products yielded at higher reaction temperatures. Since the Ti-O bond distance is larger than the Si-O bond distance these results give an indication for the insertion of Ti in the framework of highly siliceous ZSM-5. Furthermore, the changes from monoclinic unit cell symmetry in dealuminated ZSM-5 towards orthorhombic symmetry in the final products confirm this idea and are in agreement with the reported characteristics of hydrothermally prepared TS-1 [5].

Table 1
Crystal data *

Sample	framework symmetry	unit cell parameters [nm]
ZSM-5	orthorhombic	$a = 2.0131$ $b = 1.9922$ $c = 1.3410$
ZSM-5 after dealumination	monoclinic	$a = 2.0110$ $b = 1.9890$ $c = 1.3386$
dealuminated ZSM-5 after subsequent reaction with $TiCl_4$ (673 K)	orthorhombic	$a = 2.0125$ $b = 1.9912$ $c = 1.3401$
dealuminated ZSM-5 after subsequent reaction with $TiCl_4$ (773 K)	orthorhombic	$a = 2.0127$ $b = 1.9916$ $c = 1.3407$

* The XRD patterns were measured on a Philips PW 7200 spectrometer using CuKα radiation. The unit cell parameters were obtained by a least-squares fit to the interplanar spacings of 10 strong reflexions.

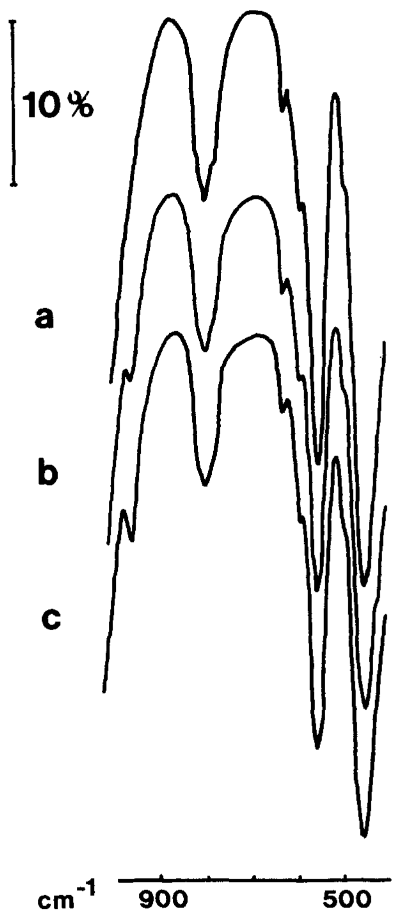

Fig. 1. IR spectra of (a) ZSM-5 after dealumination with hydrochloric acid, (b) dealuminated ZSM-5 after subsequent reaction with $TiCl_4$ at 673 K, (c) dealuminated ZSM-5 after subsequent reaction with $TiCl_4$ at 773 K. The spectra were obtained on a Hitachi 270-30 spectrometer using wafers of 0.6 mg sample in 200 mg KBr.

The infrared spectra of samples treated with $TiCl_4$ exhibit an adsorption band at 970 cm^{-1} which is absent in ZSM-5 or silicalite-1. It has been reported that this adsorption band is characteristic for TS-1 and the intensity was found to be a function of the titanium content in the lattice [5]. Therefore, the spectra in fig. 1

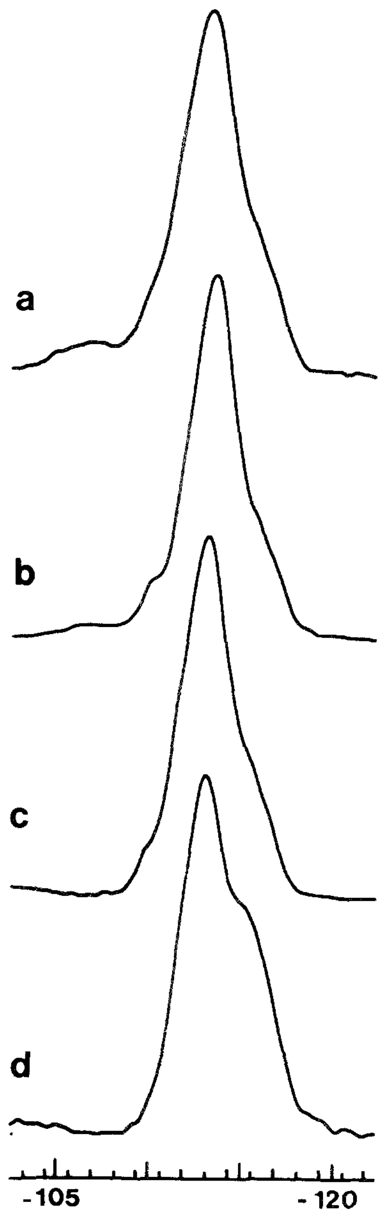

Fig. 2. ^{29}Si MAS NMR spectra of (a) ZSM-5 starting material with Si/Al = 50, (b) ZSM-5 after dealumination with hydrochloric acid, (c) dealuminated ZSM-5 after subsequent reaction with $TiCl_4$ at 673 K, (d) dealuminated ZSM-5 after subsequent reaction with $TiCl_4$ at 773 K. The spectra were obtained on a Bruker CXP-300 spectrometer at 59.63 MHz.

give a further indication for the idea that higher reaction temperatures favour the insertion of Ti.

The ^{29}Si MAS NMR spectra [6] of ZSM-5 exhibit a signal at −106 ppm (relative to TMS) due to Si(3Si, Al) structural units in the starting material and due to Si(3si, OH) structural units in the dealuminated sample [fig. 2]. Crystallographically non-equivalent Si(4Si) units are not distinguishable in the latter sample since the defect sites (silanol groups) affect the line width. As a result of the subsequent reaction with $TiCl_4$ the ^{29}Si MAS NMR signal due to silanol groups decreases and the spectra exhibit an additional shoulder at about −115 ppm which has also been reported to be typically for TS-1 [7].

We conclude that acid leaching of ZSM-5 yields highly siliceous products with vacant T-atom positions in the lattice which are available for the insertion of Ti atoms. The extend of the Ti insertion can be controlled by variation of the reaction temperature and, most probably, by the vapour pressure of $TiCl_4$ and the reaction time.

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