Variable Temperature ^{29}Si MAS NMR Studies of Titanosilicalite TS-1

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Variable temperature ^{29}Si MAS NMR spectroscopy has been used to correlate the monoclinic–orthorhombic transition temperature of titanosilicalite TS-1 with the Ti content.

The titanium molecular sieve TS-1 is a zeolite of the pentasil family where a fraction of the Si^{4+} ions are replaced by Ti^{4+} ions.[1] It has been found to be a remarkable catalyst for the oxidation of various organic substrates with hydrogen peroxide.[2] Although framework titanium ions are thought to be the active sites,[3] the nature of tnese centres is far from fully elucidated. In a sustained effort to prove the framework nature of the titanium ions, a number of physico-chemical characterizations have been used.[4]

In particular, TS-1 shows a characteristic IR pattern similar

Table 1 Designation, unit cell composition and symmetry of the different samples

Designation	Unit cell composition[a]	Symmetry at room temp.[b]
TS(0)	$Si_{96}O_{192}$	M
TS(1)	$Si_{95.59}Ti_{0.41}O_{192}$	M
TS(2)	$Si_{95.15}Ti_{0.85}O_{192}$	M
TS(3)	$Si_{94.75}Ti_{1.25}O_{192}$	O
TS(4)	$Si_{94.25}Ti_{1.75}O_{192}$	O

[a] The chemical compositions were obtained for calcined samples by usual analytical methods. Crystal size and morphology did not depend on the Si/Ti ratio. All samples were highly crystalline as shown by IR spectroscopy and XRD. The absence of non-framework TiO_2 was revealed by UV spectra recorded on a Perkin-Elmer Lambda 9 UV-VIS spectrometer. [b] Estimated from XRD patterns (peak at 2θ = 24.4°) recorded on a Philips PW 1710 diffractometer using Cu-Kα radiation. M = monoclinic, O = orthorhombic.

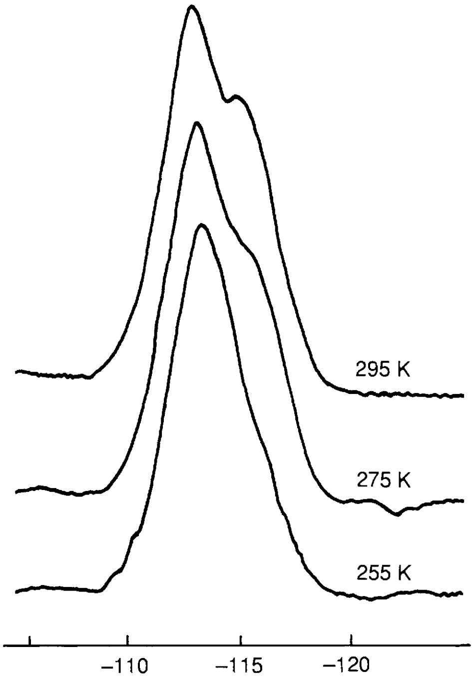

Fig. 1 ^{29}Si NMR spectra of sample TS(3) recorded at different temperatures. Spectra were recorded on a Bruker MSL 300 FT NMR spectrometer equiped with a double-bearing variable temperature MAS probehead. This equipment allowed us to work in the temperature range 173–373 K. Before acquisition, the system was left for 30 min in order to stabilize and homogenize the temperature. Spectra were collected using a classical 90° acquisition sequence. Samples were typically spun at 4 kHz. In order to minimize the effect of varying relaxation times with temperature, spectra were recorded with 20 s delay time between each scan. In most cases, 100 FID were accumulated. All chemical shifts were referenced with respect to $SiMe_4$.

to that of silicalite and, in addition, a new absorption at 960 cm^{-1}. This band, whose intensity is proportional to the Ti content of TS-1, has been attributed to a stretching mode of a $[SiO_4]$ unit bonded to a Ti^{4+} ion.[5]

^{29}Si MAS NMR spectra of calcined TS-1 exhibit a broad peak around −116 ppm *vs.* $SiMe_4$, whose intensity increases with increasing Ti content of the zeolite.[6] This peak has been interpreted as arising from distorted Si–O–Si bonds resulting from the presence of Si–O–Ti linkages.[7]

As one might conclude, none of these spectral observations could be considered as clear-cut evidence for the framework siting of titanium. This is particularly the case as Conner *et al.*[8] reported that such a band could also be observed in the ^{29}Si NMR spectra of silicalite or ZSM-5 samples, provided that the latter were recorded at temperatures over 320 K.[8]

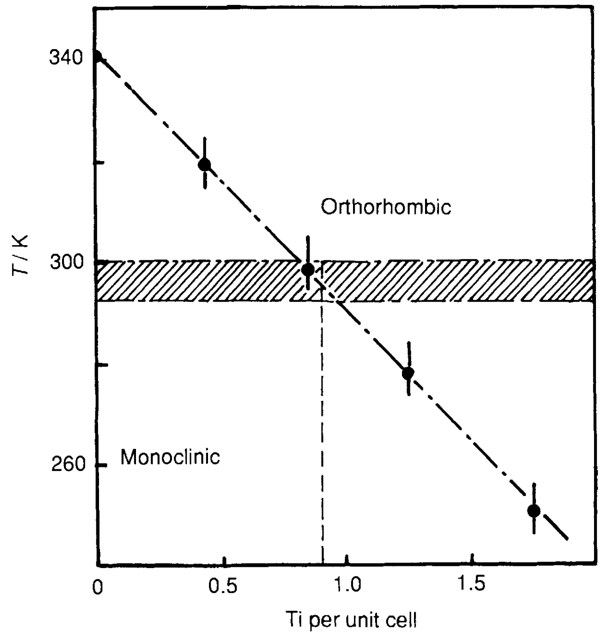

Fig. 2 Variation of the monoclinic to orthorhombic transition temperature as a function of the Ti content in the zeolite. The dashed area corresponds to ambient temperature (290–300 K).

Our purpose is to unveil a clear relationship between the nature and content of the substituting element and the transition temperature between monoclinic and orthorhombic symmetries. Such a relation would then be useful as a quantitative and qualitative tool to investigate the extent of isomorphous substitution.

TS-1 samples were synthesized following the method described by Kraushaar *et al.*[9] In order to obtain different Si/Ti ratios in the solid, the amount of tetraethylorthotitanate was varied in the synthesis mixture. As-synthesized solids were calcined in air at 550 °C for 5 h to remove the templating agent.

The unit cell composition and the crystal structure symmetry of the investigated samples are reported in Table 1. TiO_2-free TS(1) to TS(4) samples are highly crystalline and show a typical IR absorption band at 960 cm^{-1}. Samples TS(0) to TS(2) exhibit monoclinic symmetry at ambient temperature [from X-ray powder diffraction (XRD) patterns] whereas samples TS(3) and TS(4) have orthorhombic symmetry.

Fig. 1 shows typical ^{29}Si MAS NMR spectra of sample TS(3) recorded at different temperatures. At temperatures over 275 K, the spectra are similar to those reported in the literature for TS-1: namely a major resonance at −113 ppm associated with a more or less pronounced shoulder at −116 ppm. Below this temperature, the shoulder disappears and the spectra are similar to those of ZSM-5 recorded at room temperature. For the particular sample under investigation, the transition temperature, corresponding to the modifications in the NMR spectra, is centred around 275 K, *i.e.* slightly below ambient temperature. In contrast with silicalite,[10] we did not observe significant changes in the appearance of the ^{29}Si NMR spectra above and below the transition temperature, probably because of the large widths of the NMR peaks.

Each sample within the series exhibited similar behaviour; however, transition temperatures varied with the titanium content. Fig. 2 depicts the evolution of the monoclinic to orthorhombic transition temperature with the Ti content of the samples. The transition temperature of samples TS(0) to TS(4) decreased almost linearly with the Ti/Si ratio, as already observed for ZSM-5 on increasing the Al/Si ratio.[11] The transition temperature may also be affected by sorbed organic or inorganic species.[12] In the present work, careful monitoring of the synthesis parameters and post-synthesis treatment prevented the deposition of non-framework material, as proved by various means of characterization. Kokotailo *et al.*[11] reported that the monoclinic angle β increased with Si/Al ratios. Thus, β approaches 90° with increasing aluminium content and temperature, until β becomes equal to 90°, at which point the symmetry becomes orthorhombic.

High-resolution X-ray diffraction has also been used to monitor the evolution of the transition temperature with the degree of substitution. This technique allows the change in the β angle to be followed by measuring the degree of separation of the 313 and $31\bar{3}$ reflections. As an example, Gabelica *et al.*[13] have shown that the monoclinic to orthorhombic temperature varied linearly with the Ge content in Ge-substituted silicalites.

For TS-1, X-ray diffraction revealed that the monoclinic symmetry, characteristic of pure silicalite at room temperature, persisted for calcined samples at room temperature up to around 1 Ti per unit cell.[6] Variable temperature ^{29}Si MAS NMR data clearly show that our samples possess monoclinic symmetry at ambient temperature for Ti content below 0.9 Ti per unit cell (Fig. 2). This result is in good agreement with the experimental observations reported previously.

We have thus shown that a reversible monoclinic to orthorhombic transition could be observed for TS-1 samples using variable temperature ^{29}Si MAS NMR spectroscopy and that the presence of the NMR shoulder at −116 ppm *vs.* $SiMe_4$ is characteristic of substituted MFI-type zeolites having orthorhombic symmetry. The corresponding temperature of the transition decreased with increasing Ti content of TS-1, a similar behaviour to that previously reported for ZSM-5.[14]

Therefore, it is possible to use this method to investigate the extent of substitution in these materials. Indeed, the slope of the linear plot may be expected to vary with the ionic radius of the incorporated element.

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