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# Titanoxane–siloxane eight-membered rings as precursors of anatase/silica and rutile/silica materials

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The eight-membered titanium containing siloxane rings $(TiX_2)_2O_4(SiBu^t{}_2)_2$ (X = Cl **1**, Br **2** or I **3**) are efficient single-source precursors to homogeneous titania–silica material. The ceramic conversions which occur pyrolytically at about 550 °C give a mixture of $TiO_2$–$SiO_2$ materials. Differential thermal and thermogravimetric analysis, X-ray diffraction, vibrational spectroscopy as well as scanning electron microscopy were used to characterise the materials. It was found that the nature of the halogen atoms play a crucial role in the thermal transformation. Thus, after thermal treatment, silica mixed with anatase is obtained from **1** and **3**, whereas silica mixed with rutile is obtained from the brominated precursor **2**. The thermal evolution of **1** studied by using Raman and infrared spectroscopies confirms the inhibiting effect of $SiO_2$ on the anatase–rutile phase transformation. The molecular route to oxide materials described could represent an alternative to the sol–gel process and may offer certain advantages.

## Introduction

At the present time hybrid molecular systems, including fragments of both siloxane and metal oxide structures, are of great interest owing to their catalytic properties.[1] They may also be used as models for studying both the structural and physicochemical properties of metal and semiconductor surfaces modified with siloxane coatings.[2]

Considerable attention is focused on oxide materials and their preparation by the sol–gel process.[3] This very powerful synthesis method, based on hydrolysis and the condensation of metal alkoxide precursors, provides reliable routes to pure metal oxides and composite materials which may be processed into a large variety of materials (thin films, fibers, monoliths, and so on). One limitation of the sol–gel method is the need to work with fairly polar media, as aqueous or alcoholic solutions. Another problem concerns the inherent difficulty in obtaining homogeneous (atomically well mixed) multicomponent oxides, since the different metal alkoxide precursors hydrolyse at different rates, leading to homometallic M–O–M linkages and heterogeneous mixtures of oxides.[3,4]

Recently, Tilley and co-workers have investigated an alternative route to mixed-metal oxide materials, using oxygen-rich "single-source precursor" molecules which possess the basic building blocks for forming the targeted oxide material.[5] This approach is based on the initial finding that M-O-Si$(OBu^t)_3$ derivatives eliminate cleanly isobutylene and water at remarkably low temperatures (100–150 °C) to form $M_xSi_yO_z$ materials. Thus, simple tris(alkoxy)siloxide complexes seem well suited as precursors to oxide materials, since the elements to be incorporated into the structure are already initially only bonded to oxygen. This method can be used to obtain high surface area powders or thin films, and recently has been extended to the production of antireflection $TiO_2$–$SiO_2$ coatings by CVD process.[6] These conversions are non-hydrolytic, and hence can also be carried out in non-polar solvents. Other non-hydrolytic methods which have been developed for the synthesis of mixed-element oxides are based on the condensation of metal alkoxides with metal acetates[7] or with metal halides.[8]

As part of our study of compounds in which organosiloxanes are attached to transition metals, we have already reported the synthesis of several eight-membered heterocyclic siloxane rings[9] and their vibrational study by infrared and Raman spectroscopies.[10] Recently, Roesky and co-workers published a review describing the preparation and the chemical properties of various heterometallasiloxane rings.[11] The aim of the present work was to explore the stability, structure and chemical behaviour of different halogen–titanium–siloxane eight-membered rings. In this initial work we have carried out TG, DTA, Raman and X-ray diffraction studies of such compounds. To our knowledge, it is the first time that such an investigation has been conducted on these types of heterocycle.

## Experimental

### Materials

The compounds were synthesized by using a simple condensation reaction between di-*tert*-butylsilanediol $Bu^t{}_2Si(OH)_2$ , and $TiCl_4$, $TiBr_4$, $TiI_4$ metal halides in polar solvents.[9a] The di-*tert*-butylsilanediol was first prepared by the Weidenbruch

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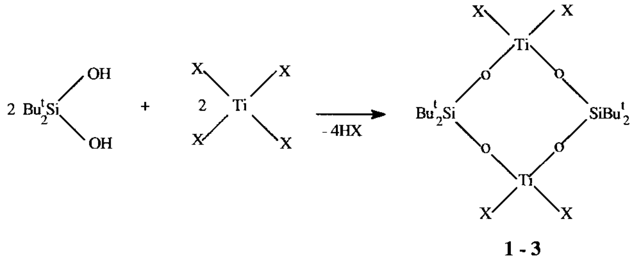
process.[11] By the use of this ligand, all the heterocyclic compounds **1**, **2** and **3** were synthesized according to the following condensation reaction:



**1 - 3**

| | 1 | 2 | 3 |
|---|---|---|---|
| X | Cl | Br | I |

## Methods

The thermal behaviour of the different compounds has been investigated by using several complementary techniques. Simultaneous TG–DTA experiments were performed in air in platinum crucibles with a Setaram TG 92/1600 Instrument using a 10 °C min$^{-1}$ heating–cooling rate. X-Ray thermodiffractometry studies were carried out using a Guinier–Lenné Camera (gold grid sample holder; 10 °C h$^{-1}$ heating rate). The materials were deposited on the sample holders using an ethanol slurry which yields, upon evaporation, a regular layer of powdered sample. Electron microprobing and microanalysis (EMMA) were performed on an automatic CAMECA-MICRO microprobe allowing elemental analysis and X-ray maps.

Raman spectra were recorded using a DILOR LABRAM multi-channel Raman microspectrometer. The 632.8 nm radiation from a helium–neon laser was used for excitation. The spectral resolution was 8 cm$^{-1}$ and the band positions were accurate to $\pm 1$ cm$^{-1}$. The Raman microspectrometer used allowed us to analyse very small amounts of sample. More particularly, using a long working distance microscope objective, we were able to record directly through the glass wall the Raman spectra of micro-crystals stuck on the inner wall of the small sealed Pyrex tubes containing the samples. Infrared spectra were recorded using a Bruker IFS 88 FT infrared spectrometer. The spectral resolution was 2 cm$^{-1}$ and the band positions were accurate to $\pm 0.1$ cm$^{-1}$.

Solid-state MAS $^{29}$Si NMR spectra were recorded on a Bruker ASX 100 FT-NMR spectrometer at 19.89 MHz using tetramethylsilane as an external reference. Room temperature wide-line solid-state $^{49}$Ti NMR spectra were obtained by using a Bruker 400ASX-FT NMR spectrometer at a frequency of 22.56 MHz, using a modified 7 mm MAS probe, with spinning. Chemical shifts are referenced to the $^{49}$Ti resonance of external $TiCl_4$. Spectra were obtained with a 138 µs echo delay, pulse repetition time of 0.5 s and accumulation of approximately 432000 scans. The pulse widths used were typically 4.2 µs for the 90° pulse and 8.4 µs for the 180° pulse. The measurements were made on a static sample at room temperature.

## Results and discussion

Thermogravimetric curves obtained for compounds **1**, **2** and **3** are shown Fig. 1. They reveal many interesting features. The onset of the first decomposition begins at slightly different temperatures for the different compounds, indicating different degrees of thermal stability for the heterocycles. Thus, the heterocycles containing iodide groups appears to be the most stable, while the brominated one is the least stable. TG curves also reveal an approximate two-stage decomposition for all compounds but their mode of decomposition seems quite different. Thus, **1** and **2** exhibit relatively sharp and well defined decomposition stages suggesting that the compounds formed at this stage are stable and may probably be isolated, while the TG curve for compound **3** shows a dramatic weight loss beginning around 300 °C. For all compounds, the decomposition is complete for a temperature close to 550° C, resulting in a ceramic yield of 48.6% (47.7) for **1**, 36% (36.6) for **2** and 28% (29.4) for **3** (the values in parenthesis represent the theoretical ceramic yield assuming 1 mol of siloxane eight-membered ring decomposes to give 2 mol of $SiO_2$ and 2 mol of $TiO_2$). The DTA curves for compounds **1**, **2** and **3** exhibit a broad exotherm around 550 °C associated with their decomposition, along with two endotherms (at 220 and 270 °C for **3**) and three weak endotherms (at 80, 140 and 270 °C for **2**). The phase transitions and/or chemical changes associated with most of these endotherms have not yet been characterised, but the endotherms at 270 °C would seem to be associated with the melting of compounds **2** and **3**.

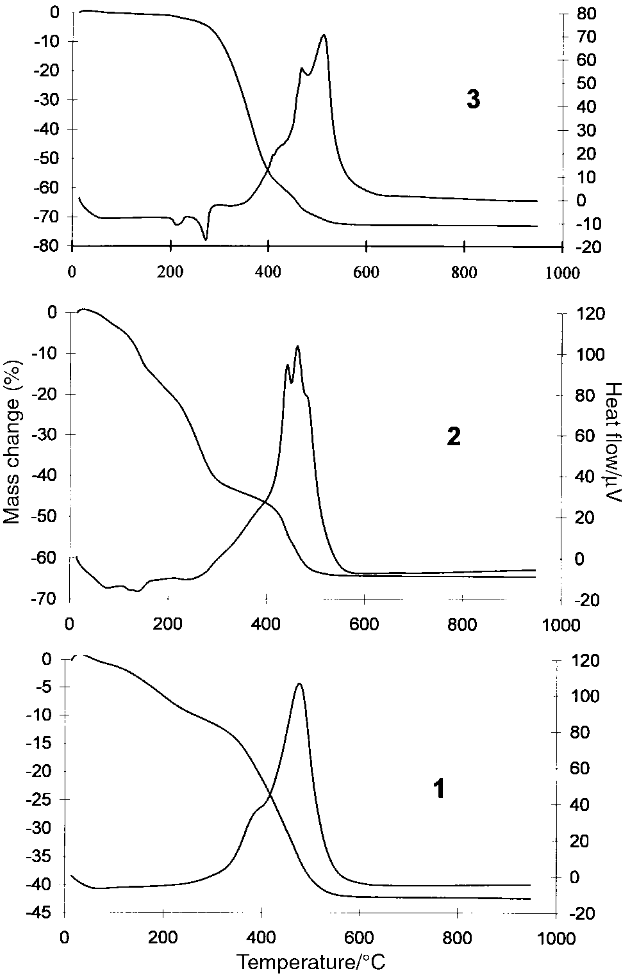


**Fig. 1** TG/DTA curves for compounds **1** ($C_{16}H_{36}Cl_4O_4Si_2Ti_2$), **2** ($C_{16}H_{36}Br_4O_4Si_2Ti_2$) and **3** ($C_{16}H_{36}I_4O_4Si_2Ti_2$).

As might be expected by comparison with the behavior of the $OSi(OBu^t)_3$ precursor, the presence, for all compounds, of Bu$^t$Si groups on the one hand, and of an eight-membered ring structure on the other, results in a greater stability for the precursors as well as a gradual conversion towards the final ceramic compound. This fact is evidenced by the TGA curves for compounds **1**, **2** and **3**, which show that the onset temperature of decomposition is just below 550 °C. By contrast, Tilley and co-workers[5] reported that the decomposition occurs at a much lower temperature (150 °C) when tris(*tert*-butoxy)siloxy complexes are used as single-source precursors for the synthesis of the homogeneous metal–silica materials.

Crystallisation is an exothermic phenomenon which is easily detected by DTA–TG techniques. Thus, we have attributed the strong exothermic peak observed around 550 °C on the thermograms of all compounds to the crystallisation of the residual compounds after decomposition. Most of the studies done on the crystallisation of amorphous powders were made by using X-ray diffraction (XRD) which is a technique known to be sensitive to long-range (50–100 Å) order. However, in many cases, the thermal evolution of amorphous materials, including $TiO_2$,[12–17] has been followed using Raman spectroscopy, which is known to be more sensitive to shorter-range order than XRD. We have applied this technique to the study of the residues obtained after the thermolysis of compounds **1**, **2** and **3**.

These Raman spectra reveal many interesting features. In particular, the spectra of the residues obtained from compounds **1** and **3** are characteristic of anatase $TiO_2$ (lines at 639, 516, 397 and 144 $cm^{-1}$),[18–22] whereas the spectrum of the residue obtained from **2** is characteristic of rutile $TiO_2$ (lines at 612, 448 and 240 $cm^{-1}$).[9,20,22] No extra bands corresponding to silica were found but, it is well known that the Raman bands associated with Si–O and Si–O–Si modes in amorphous silica are always very weak. These spectroscopic data suggest that the decomposition at relatively low temperature (550 °C) of compounds **1**, **2** and **3** leads to mixtures of titanium oxides with amorphous silica (the formation of silica although not detected by Raman spectroscopy has, however, been evidenced by EMMA and IR spectroscopy as described below). After many experiments, it was systematically observed that the decomposition of compounds **1** and **3** leads exclusively to the formation of anatase while that of compound **2** leads exclusively to the formation of rutile. However, the mechanism of the thermal conversion of the heterocycles into materials containing silica and titanium oxide has not, until now, been elucidated. Nevertheless, we assume that the common intermediates of all compounds could be the partially hydrolysed halogenated heterocyles. Indeed, the TG–DTA curves corresponding to the partially hydrolysed compound **1** (the hydrolysis occurring in static air for 1 day) reveal, besides the exothermic decomposition peak around 550 °C, a strong endothermic peak at 100 °C, which could be assigned to the dehydration of the partially hydrolysed compound. The Raman spectra corresponding to the silica–titanium oxide powder obtained after the thermal treatment of compound **1** at 550 °C is characteristic of crystalline anatase as mentioned above.

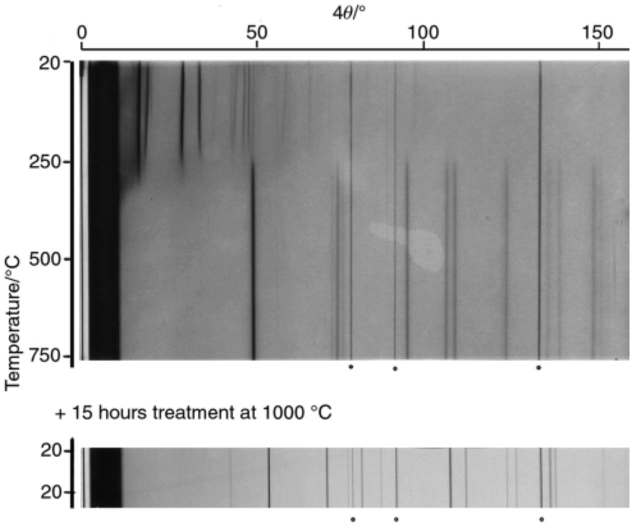


**Fig. 2** Guinier–Lenné X-ray diffraction patterns of the residue of compound **1** (a) after thermal treatment at 550 °C and (b) after 15 hours treatment at 1000 °C. Pt reflections of the sample holder grid are noted by black points (●).

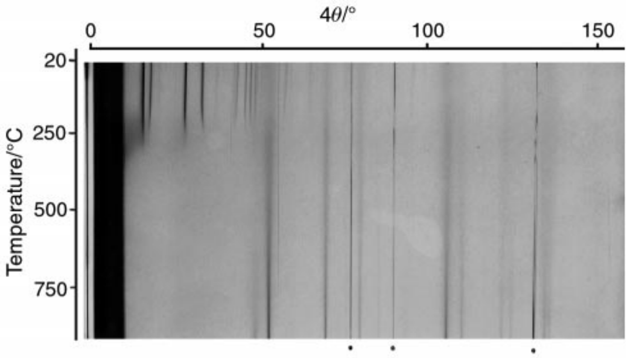


**Fig. 3** Guinier–Lenné X-ray diffraction patterns of the residue of compound **2** after thermal treatment at 550 °C. Pt reflections of the sample holder grid are noted by black points (●).

The Guinier–Lenné X-ray patterns of compounds **1** (Fig. 2a) and **2** (Fig. 3) were obtained with a 20 °C $h^{-1}$ heating rate. These X-ray diffraction patterns reveal that the pyrolysis products derived from compounds **1** and **3** annealed at 550 °C contain crystalline $TiO_2$ exclusively in the anatase form, whereas rutile is the only crystalline form of $TiO_2$ derived from **2** and annealed at the same temperature. This observation is fully consistent with results obtained by Raman spectroscopy.

Electron microprobing and microanalysis was used to analyse the morphology and composition of the residues resulting from the thermal decomposition of the compounds **1**, **2** and **3**. X-Ray elemental analysis shows that all the residues are effectively $TiO_2$–$SiO_2$ mixtures. Moreover, secondary electron photomicrographs as well as X-ray maps (obtained from Si and Ti Kα lines) show that these residues present quite different characteristic morphologies. The residues obtained from compounds **1** and **3** are heterogeneous mixtures of two compounds: (i) crystalline aggregates with fine granular appearance containing Ti (identified by X-ray) which correspond to $TiO_2$ anatase (identified by Raman), (ii) amorphous phases containing Si (identified by X-ray) which correspond to $SiO_2$. On the other hand, the residues obtained from compound **2** are a rather homogeneous agglomeration of uniform size small grains containing either Ti (identified by X-ray) which corresponds to rutile $TiO_2$ (identified by Raman) or Si (identified by X-ray) which corresponds to $SiO_2$.

The $^{29}Si$ MAS-NMR spectra were recorded from the residue obtained after thermal decomposition of compound **1** at 550 °C. This material gives rise to a broad envelope of resonances centred at –110.2 ppm. This result is in agreement with those reported by Tilley *et al.*[5] obtained from similar $MO_2$–$SiO_2$ (M = Ti, Zr or Hf) materials. Unfortunately, only a few solid-state Ti NMR studies have been published to date.[23] The reasons for this lack of solid-state Ti NMR studies are that the magnetically active nuclei, $^{47}Ti$ and $^{49}Ti$, have low natural abundances, small magnetogyric ratios, and large nuclear quadrupole moments. Thus, the intrinsic sensitivity is low and the resonance lines are usually very broad. However, a paper on titanium solid-state NMR of anatase, brookite and rutile has recently been published[24] which argues that solid-state Ti NMR spectroscopy could be a useful tool for the characterisation of the structure and the catalytic behaviour of Ti in interstitial Ti-site-isolated catalysts as well as a useful aid in structural studies of other titanium-containing solids. In this regard, we have attempted to record $^{49}Ti$ MAS-NMR spectra from the same residue. These spectra exhibit a very broad resonance line centred at 432.2 ppm. This is not surprising since the titanium atoms in anatase are in non-cubic symmetry sites and, consequently, the second-order quadrupolar effects should dominate the NMR spectra.

It is known that there exist three titanium oxide polymorphs (tetragonal anatase and rutile, orthorhombic brookite). Anatase and brookite can irreversibly be transformed into rutile by heating[25–29] or even by mechanical methods. There are a great number of studies dealing with the effect of the presence of impurities on the anatase–rutile transformation.[27–29] Indeed, this transformation is known to be influenced markedly by the nature and the amount of impurities present in the system. It has been reported that the addition to anatase of $Li^+$, $Cu^{2+}$, $Co^{2+}$, and $Mn^{4+}$ oxides or fluorides improves the transformation,[27,28] while the presence of impurities like $Nb_2O_5$, $PO_4{}^{3-}$, $SO_4{}^{2-}$ and $SiO_2$ renders it more difficult.[27,29] In most cases the phenomenon is interpreted in terms of a defect structure mechanism.[28] Thus, in order to confirm that the presence of silica has an inhibiting effect on the anatase–rutile phase transformation, we have recorded the Raman spectra of the partially hydrolysed compound **1** heated at different temperatures in an oven for 2 hours under static air atmosphere. Fig. 4 shows the Raman spectra obtained after heating at 100, 400, 600, 800, 1000 and 1200 °C. These indicate clearly that the $TiO_2$ anatase is formed but that no phase transformation occurs between 400 and 800 °C. At 1000 °C a small band is observed at 448 $cm^{-1}$ which indicates that a small amount of rutile has formed at this temperature. Since the phase transformation normally occurs above 600 °C this confirms the inhibiting effect of silica. As expected, at 1200 °C, only the rutile spectrum is observed indicating that the transformation of the anatase into rutile is now complete.

From the X-ray diffraction patterns (Fig. 2b) it can be seen that the anatase–rutile transformation has taken place in sample **1** annealed at 1000 °C for 15 hours.

In order to obtain more information on the thermal phase transformation of $TiO_2$, we also recorded the IR spectra, in KBr pellets, of compound **1** heated at different temperatures in the 100–1200 °C range. All the spectra in the 600–200 °C range exhibit, after subtraction of the spectrum of $TiO_2$, bands characteristic of $SiO_2$ (Fig. 5). In particular, the spectra recorded at 600, 800, 1000 and 1200 °C exhibit a large band centred at 1060 $cm^{-1}$ which shifts to 1100 $cm^{-1}$ at high temperature. This band corresponds well to the Si–O asymmetric stretching mode of amorphous silica.[30] These data along with those obtained by EMMA confirm that amorphous silica, though not detected by Raman spectroscopy, is always present in the residues obtained after thermal decomposition of compounds **1**, **2** and **3**.

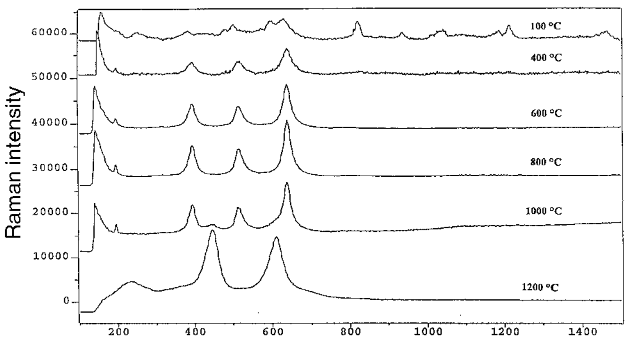


**Fig. 4** Raman spectra obtained after heating of compound **1** at 100, 400, 600, 800, 1000 and 1200 °C.

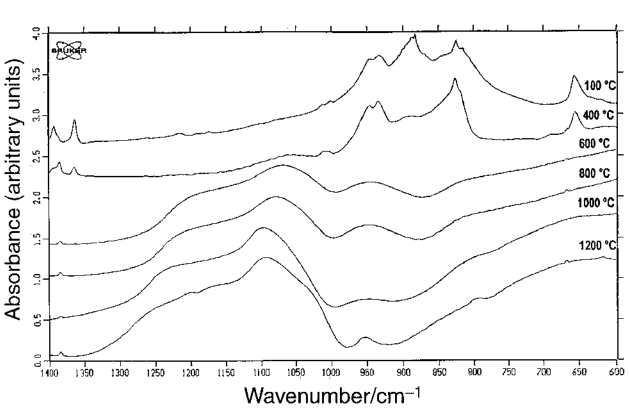


**Fig. 5** FT IR spectra obtained after heating of compound **1** at 100, 400, 600, 800, 1000 and 1200 °C.

## Conclusion

The thermal transformation of compounds **1**, **2** and **3** into ceramic materials represents a new synthesis route for the formation of titania–silica materials. The solid-state transformation of **1** and **2** leads to relatively heterogeneous structures. By contrast, those of compound **2** leads to relatively homogeneous structure. However, the mechanism of these transformations is, at present, still unclear. By changing the nature of the halogen atoms, it is possible to prepare either a silica–$TiO_2$ anatase mixture or a silica–$TiO_2$ rutile mixture. Surprisingly, the rutile phase can directly be synthesized at low temperature (550 °C) from the brominated precursor. We have also studied the thermal anatase–rutile transformation in the presence of silica, which confirms the results of a previously reported study indicating the inhibiting effect of a silica support on this transformation.

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