

Letter

# Sulfur dioxide as a chemical probe for titanyl groups in titanium silicalites

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Received 14 March 1996; accepted 21 March 1996

## Abstract

The reaction of titanyl (Ti=O) groups with SO<sub>2</sub>, which for molecular titanyl complexes is found to occur readily at room temperature, has been used to test for the presence of titanyl groups in titanium silicalite (TS-1) and Ti-MCM-41. Exposure of samples to SO<sub>2</sub> does not lead to any reduction in the intensity of the characteristic IR band observed at 960 cm<sup>-1</sup>, implying that this absorption is not associated with the presence of titanyl groups.

*Keywords:* Titanium; Silicalite; TS-1; Ti-MCM-41; Active site

## 1. Introduction

The discovery of the synthetic titanium-containing zeolite TS-1 in 1983 represents one of the most significant developments in the area of oxidation catalysis in recent years. TS-1 possesses an MFI structure in which Si is isomorphously substituted by Ti up to a limiting molar Ti/(Ti + Si) ratio of around 0.025–0.04 [1]. Of particular scientific and commercial interest are the catalytic properties of TS-1: using H<sub>2</sub>O<sub>2</sub> as oxidant, TS-1 is active in a variety of oxidation reactions such as the epoxidation of olefins, the hydroxylation of aromatics, the oxidation of paraffins to alcohol/ketone mixtures, and the ammoxidation of ketones [1]. The remarkable properties of TS-1 have in turn led to research

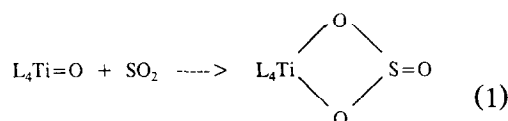
directed at the synthesis of large and ultralarge pore Ti-zeolites [2,3].

In its IR spectrum, TS-1 shows a characteristic absorption band at about 960 cm<sup>-1</sup> which is not present in the pure silicalite spectrum, and is absent in titanium oxides (rutile, anatase) and alkaline titanates. Significantly, the position of this band is similar to that found for amorphous titania-on-silica epoxidation catalysts, for which it has been proposed that the active site comprises surface titanyl groups (Ti=O) [4]. On this basis it has been suggested that the active site in TS-1 may likewise correspond to a titanyl group [5]. Support for this type of titanium site is provided by published IR spectral data on molecular titanyl complexes, which characteristically show an absorption band in the region 980–930 cm<sup>-1</sup> [6]. However, Zecchina and co-workers [7] have argued that the 960 cm<sup>-1</sup> absorption of TS-1 corresponds to a vibration

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associated with framework  $[\text{TiO}_4]$  and  $[\text{TiO}_3\text{OH}]$  units or  $[\text{SiO}_4]$  and  $[\text{SiO}_3\text{OH}]$  units perturbed by the presence of Ti (or possibly a mixture of the two), and as such is representative of tetrahedrally coordinated Ti lattice sites. Furthermore, recent studies employing a variety of other analytical techniques have provided strong evidence that the titanium in TS-1 is located chiefly at tetrahedral lattice sites [1]. Nevertheless, these findings do not rule out the possibility that titanyl groups might be present in titanium silicalites in low concentration, or that they might possess high intrinsic activity for oxidation catalysis.

In this context it is of note that recent work by Geoffroy and co-workers [8] has established that the nucleophilic titanyl group readily reacts with electrophiles such as  $\text{SO}_2$ :



$\text{L}_4$  = macrocyclic N-donor ligand

On the basis of this result,  $\text{SO}_2$ , in combination with IR spectroscopy, would appear to be an excellent probe for the presence of titanyl groups,  $\text{SO}_2$  itself possessing no vibrations below  $1100 \text{ cm}^{-1}$ . In the following we detail the results of experiments designed to test for the presence of titanyl groups in TS-1 and Ti-MCM-41.

## 2. Experimental

### 2.1. Materials

TS-1 and Ti-MCM-41 were synthesized according to published procedures [1,3].

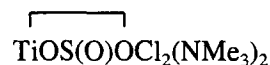
### 2.2. Reaction of $\text{TiOCl}_2(\text{NMe}_3)_2$ with $\text{SO}_2$

$\text{SO}_2$  was bubbled through a solution of  $\text{TiOCl}_2(\text{NMe}_3)_2$  (1.49 g, 5.9 mmol) in  $\text{CH}_2\text{Cl}_2$

(60 ml) under argon (note: the titanium complex is not completely soluble at this concentration), resulting in the immediate formation of a cream-coloured flocculant precipitate and evolution of heat. After 10 mins. the  $\text{SO}_2$  purge was removed and the mixture vacuum-filtered, affording a cream-coloured solid and a yellow filtrate. The solid was washed with  $\text{CH}_2\text{Cl}_2$  until the washings were almost colourless ( $6 \times 20 \text{ ml}$ ), after which solvent was removed from the combined filtrate and washings under vacuum to afford lemon yellow microcrystals, identified as



(0.34 g, 18%) (Found: C, 22.5%; H, 5.6%; N, 8.6%; S, 9.9%; Cl, 22.3%.  $\text{C}_6\text{H}_{18}\text{N}_2\text{SCl}_2\text{O}_3\text{Ti}$  requires C, 22.7%; H, 5.7%; N, 8.8%; S, 10.1%; Cl, 22.4%). IR:  $\nu_{\text{max}}/\text{cm}^{-1}$  1205, 910, 812 and 777 (SO). IR and elemental analysis of the insoluble cream solid isolated from the reaction showed it to be a mixture of starting material and



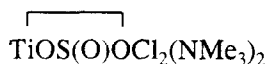
### 2.3. IR measurements

Infrared spectra were recorded on thin self-supporting wafers, diameter 18 mm, prepared from 25 mg of sample. Zeolite samples were first outgassed ( $10^{-5}$  mbar) in the spectrometer with heating ( $200^\circ\text{C}$ ) for 2 h; spectra were subsequently recorded at room temperature. Wafers of  $\text{TiOCl}_2(\text{NMe}_3)_2$  were prepared in a glove-box under nitrogen and were outgassed at room temperature in the spectrometer. Typically,  $\text{SO}_2$  (ca. 7 mbar) was introduced into the sample cell and a spectrum recorded after a period of 15 mins. The cell was then opened to

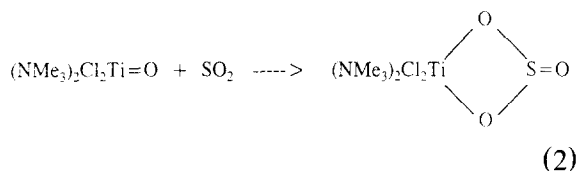
dynamic vacuum and a new spectrum recorded after a further 15 mins. All measurements were performed using a Mattson Cygnus 100 spectrometer at a resolution of  $2\text{ cm}^{-1}$ .

### 3. Results and discussion

In order to first confirm the generality of reaction (1), the reaction of  $\text{SO}_2$  with the titanyl complex  $\text{TiOCl}_2(\text{NMe}_3)_2$  ( $\nu_{\text{Ti}=\text{O}}\ 974\text{ cm}^{-1}$ ) [9] was studied. Bubbling  $\text{SO}_2$  through a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{TiOCl}_2(\text{NMe}_3)_2$ , followed by work-up, led to the isolation of



, identified by elemental analysis and IR spectroscopy:



Consistent with reaction of the titanyl group was the absence of the  $\text{Ti}=\text{O}$  absorption band in the IR spectrum of the product, while new bands were observed at  $1205\ (\nu_{\text{S}=\text{O}})$  [10] and  $910, 812$  and  $777\text{ cm}^{-1}$ . By analogy with published IR spectra of dialkyl sulfites, the latter absorption bands are assigned to vibrations associated with the  $\text{S}-\text{O}-\text{Ti}$  linkage [10].

Similarly, exposure of a solid pill of  $\text{TiOCl}_2(\text{NMe}_3)_2$  to  $\text{SO}_2$  (8 Torr) at room temperature resulted in a rapid decrease in the intensity of the  $974\text{ cm}^{-1}$   $\text{Ti}=\text{O}$  band, by a factor of ca. 60% (Fig. 1); presumably material in the centre of the pill was inaccessible to the gas on the time scale of the experiment, with the consequence that complete disappearance of

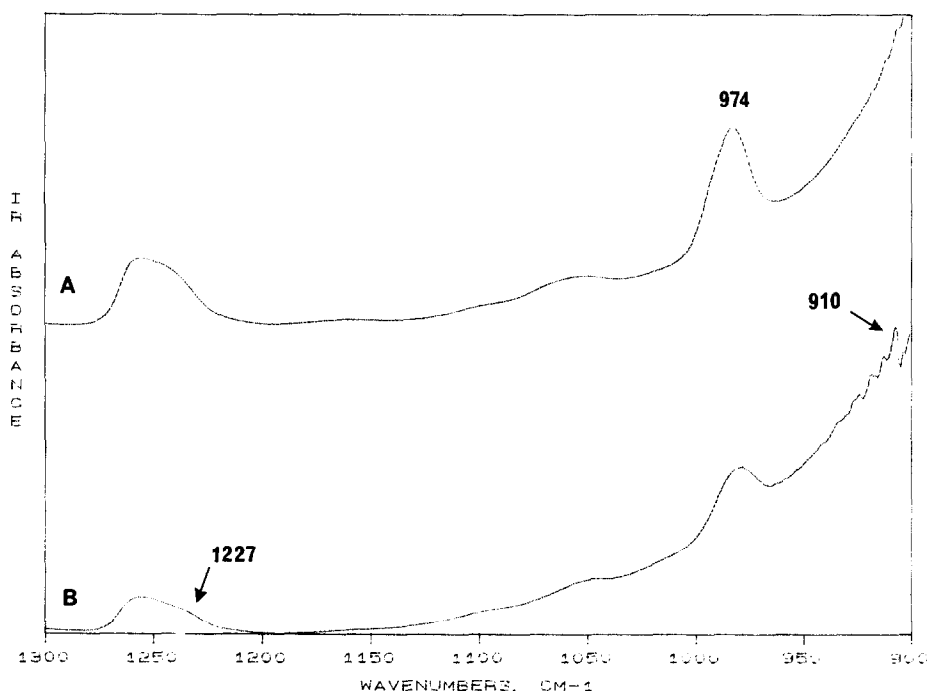


Fig. 1. IR spectrum of  $\text{TiOCl}_2(\text{NMe}_3)_2$  before (A) and after (B) exposure to  $\text{SO}_2$ .

the band was not observed. Simultaneously, new bands were observed at 1227 and 910  $\text{cm}^{-1}$ . These changes were found to be irreversible: thus exposure of the sample to dynamic vacuum ( $10^{-6}$  mbar) did not result in any increase in the intensity of the 974  $\text{cm}^{-1}$  band.

In order to perform the same experiment with TS-1, a sample was prepared containing 2.4 mol% Ti (calculated as  $\text{TiO}_2$ ). In contrast to the above, exposing the TS-1 sample (after first drying at 200°C under high vacuum) to  $\text{SO}_2$  under the same conditions did not affect the intensity or position of the band at 960  $\text{cm}^{-1}$  (Fig. 2), thereby providing strong evidence that this band does not correspond to a titanyl group. Furthermore, no new bands were observed in the region 700–1500  $\text{cm}^{-1}$ , other than those attributable to  $\text{SO}_2$ , indicating that no Ti–S linkages were formed. Similarly, exposure of a Ti-MCM-41 sample containing 1.8 mol% Ti to  $\text{SO}_2$  failed to produce any changes in the broad absorption band observed at 960  $\text{cm}^{-1}$ .

The apparent elusiveness of surface titanyl groups can be attributed to the extreme Lewis acidity of such a three-coordinate Ti(IV) center, rendering it highly reactive. 1,2-addition reactions of the Ti=O group, with, for example, water or SiOH groups, would be expected provide a facile pathway to 4-coordinate species lower in energy. Similar reasoning can be used to explain the elusiveness of siloxide groups, Si=O, on the silica surface. Indeed preliminary calculations performed in our laboratory [11], employing a Density Functional Theory (DFT) quantum chemistry method, indicate that the hydrated form of the titanyl group, as represented by the model complex  $\text{Ti}(\text{OH})_4$ , is more stable than its non-hydrated congener,  $\text{Ti}(\text{O})(\text{OH})_2$ , by approximately 43 kcal/mol. This result suggests that it is unlikely that titanyl groups could be present in significant concentrations in titanium-containing silicalites and still less under oxidising conditions (when protic species are present).

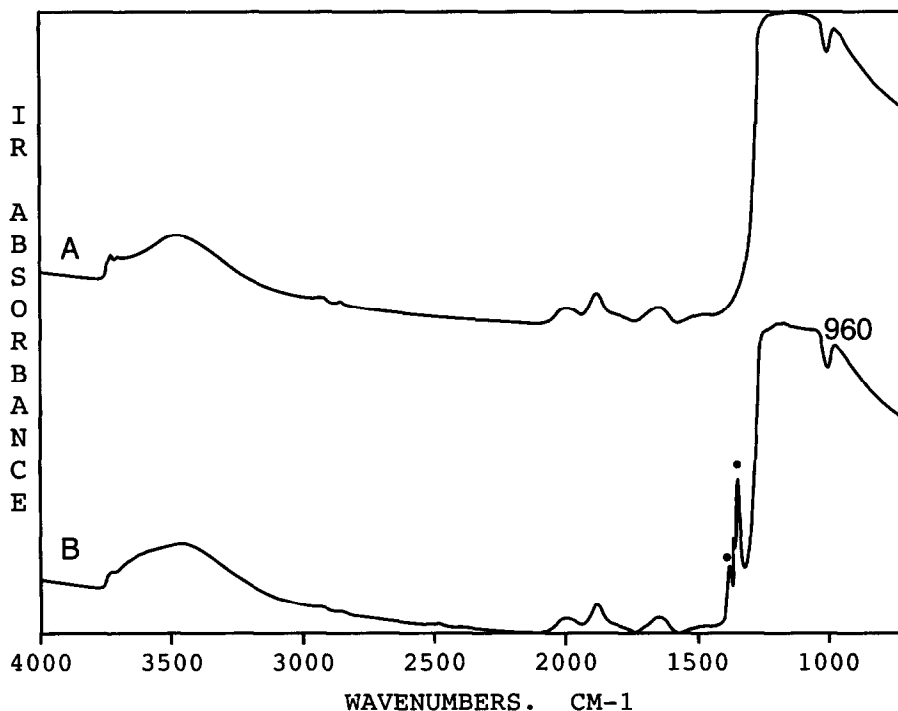


Fig. 2. IR spectrum (700–4000  $\text{cm}^{-1}$ ) of TS-1 before (A) and after (B) exposure to  $\text{SO}_2$  (● denotes band attributed to  $\text{SO}_2$ ); the broad shoulder at 3600  $\text{cm}^{-1}$  in spectrum B is assigned to the O–H stretch of silanol groups interacting with physisorbed  $\text{SO}_2$ .

In summary, our experiments indicate that titanyl groups are not present in detectable concentrations in titanium-containing silicalites. In our view the  $960\text{ cm}^{-1}$  absorption band found in IR spectra of these materials can be assigned in all cases to a Si–O–Ti stretching mode of titanium occupying lattice positions.

### Acknowledgements

The authors thank Prof. H. van Bekkum for providing the Ti-MCM-41 sample.

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