Observation of a 390-nm Emission Band Associated with Framework Ti in Mesoporous Titanosilicates

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A mesoporous titanosilicate lacking titanol groups has been prepared by exhaustive OH silylation and characterized by ^{29}Si NMR, by XANES, and by its catalytic activity for cyclohexene epoxidation. Through a comparison of the luminescence of this silylated Ti−MCM-41 titanosilicate with that of the original Ti−MCM-41 before and after calcination, firm experimental support that an emission band appearing at $\lambda_{max} = 390$ nm is due to the tetrapodal framework $Ti(OSi{\equiv})_4$ is provided.

Introduction

Titanium-containing zeolites and related mesoporous titanosilicates are important heterogeneous catalysts for the epoxidation of alkenes and hydroxylation of arenes.[1−3] The optimum catalytic efficiency of these solids is related to the presence of isolated framework Ti atoms. Because of this, it is important to develop simple experimental techniques that can report on the different Ti environments present in the solid. This information would be extremely valuable in elucidating the relationship between structure and activity, and it would help in the attainment of titanosilicates with the highest catalytic performance. In the case of Ti-containing mesoporous materials, it is well-established that the preparation procedure and Ti content play a significant role in the activity.[4] It is believed that changes in activity are due to variations in the populations of Ti atoms among different sites exhibiting distinctive catalytic activities.

Pioneering reports on the use of photoluminescence have shown that Ti atoms anchored on aluminosilicates exhibit two emission bands at $\lambda_{max} \approx 430$ and 490 nm.[5−8] It has been proposed that these bands correspond to emitting Ti atoms having different coordination spheres. On the basis of the weak luminescence in solution of $Ti[OSi(CH_3)_3]_4$, which appears at about 500 nm, the emission at 490 nm was assigned to Ti atoms in a "closed" $Ti(OSi{\equiv})_4$ coordination,[5] while, by exclusion, the 430-nm luminescence was then thought to correspond to titanols $[Ti(OH)_x(OSi{\equiv})_{4-x}$, $x = 1, 2]$.

However, mesoporous Ti−MCM-41 titanosilicates prepared by titanocene grafting and positively containing titanol groups also exhibits the 490-nm emission band.[6] This apparently does not fit well with the assignment based on the weak $Ti[OSi(CH_3)_3]_4$ emission.

To provide new experimental data on the emission spectra of titanosilicates, herein we have prepared a well-characterized mesoporous titanosilicate modified by postsynthesis procedures to have the minimum achievable population of titanol groups. Given that emission spectroscopy does not provide enough structural information about the luminescent sites, our approach has been to characterize the samples by alternative spectroscopic techniques and subsequently to correlate these with the sample emission.

Results and Discussion

A Ti−MCM-41 sample prepared by direct Ti incorporation during the synthesis was obtained as reported,[9] and the quaternary ammonium template agent decomposed by calcination at 540 °C for 6 h (Ti−MCM-41calc). Subsequently, the sample Ti−MCM-41calc was submitted to exhaustive silylation using hexamethyldisilazane as the silylating agent (Ti−MCM-41sil) (Scheme 1). After silylation, the resulting pore size of Ti−MCM-41sil showed a decrease with respect to that of Ti−MCM-41calc because of the presence of trimethylsilyl groups in the mesopores. Some relevant analytical and textural data for Ti−MCM-41 are summarized in Table 1.

These samples were characterized by ^{29}Si NMR spectroscopy (Figure 1), wherein a dramatic reduction of the Q_3 signal (−100 ppm) associated with the presence of silanol groups was observed for Ti−MCM-41sil, accompanied by a new signal at 14 ppm due to the Si

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Scheme 1

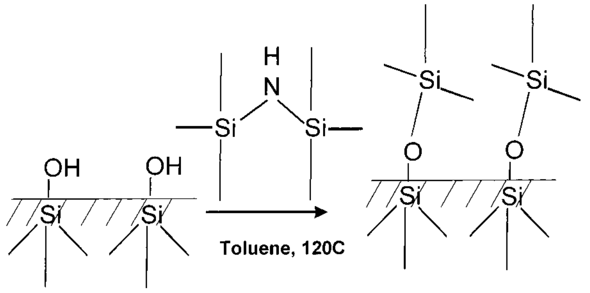

Table 1. Relevant Analytical Porosity Parameters of the Ti-Containing Samples Used in This Work

sample	a_0 (Å)	pore size[a] (Å)	BET surface area[b] (m^2/g)	pore volume[b] (cm^3/g)
Ti−MCM-41[c]	47.1	–	–	–
Ti−MCM-41calc	44.8	38	884	0.67
Ti− MCM-41sil	45.3	33	805	0.44

[a] Calculated from the Ar adsorption isotherm applying the Horwath−Kawazoe method. [b] Calculated from the N_2 adsorption isotherm. [c] Ti content, 2 wt %, expressed as TiO_2.

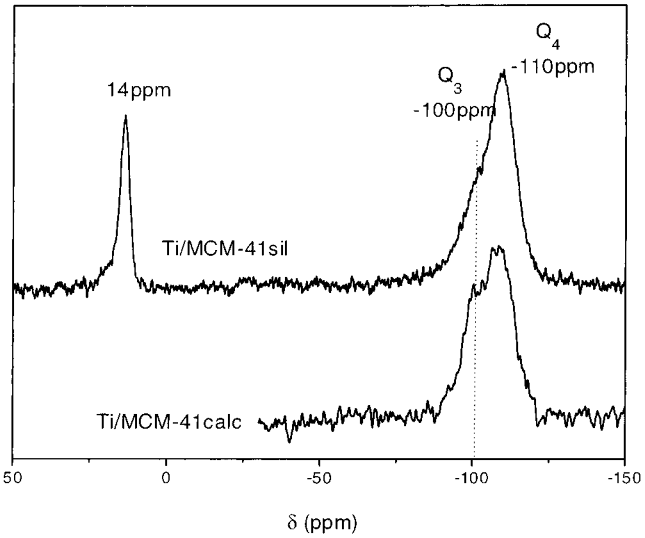

Figure 1. Solid-state ^{29}Si NMR spectra of Ti−MCM-41calc and Ti−MCM-41sil. Q_3 indicates the presence of silanols that are largely reduced upon silylation. The 14 ppm signal is due to the trimethylsilyl groups.

atoms of trimethylsilyloxy groups. In contrast, Ti−MCM-41calc showed the characteristic ≡SiOH (Q_3) resonance at −100 ppm. Also, the IR spectrum of Ti−MCM-41calc exhibited a very intense OH streching absorption band at ~3700 cm^{-1}, indicating the presence of a large population of free silanol groups, which strongly decreased in intensity upon silylation on Ti−MCM-41sil sample. Given that both Ti and Si atoms occupy framework positions, it is assumed that titanol and silanol groups are simultaneously present or absent in the calcined or silylated sample, respectively.

The Ti environment in the titanosilicates was studied by UV−vis spectroscopy (Figure 2). All of the samples had in common the appearance of an intense LMCT band at 235 nm, indicating the presence of Ti atoms in isolated sites. Additional information was provided by X-ray absorption spectroscopy in the near-edge region (XANES). XANES spectra of titanosilicate have been shown to provide important information about the tetrahedral/octahedral coordination of Ti atoms.[10−12] The XANES spectra of Ti−MCM-41calc and Ti−MCM-41sil are shown in Figure 3 in the hydrated and dehydrated forms, and the main features of the Ti preedge peaks of the Ti−MCM-41 catalysts are summarized in Table 2.

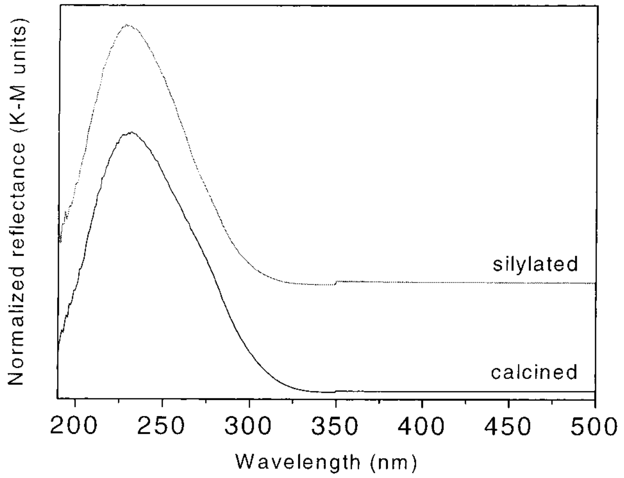

Figure 2. Diffuse reflectance UV−vis spectra (plotted as the Kulbelka−Munk function K. M.) of the Ti−MCM-41 samples in the calcined and silylated forms.

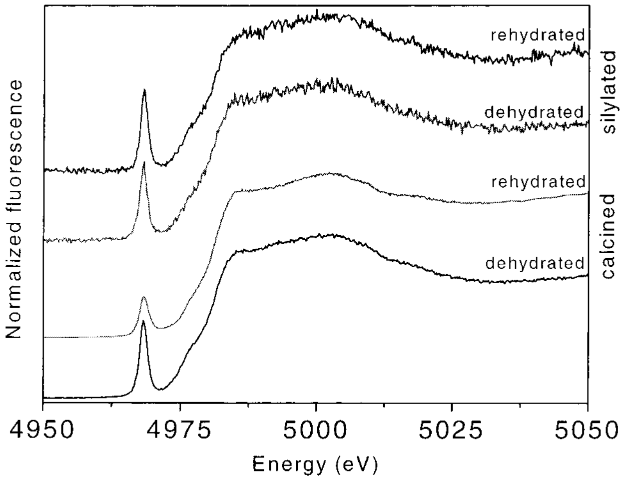

Figure 3. XANES spectra of the Ti−MCM-41 samples in the calcined and silylated forms upon dehydration and after exposure to the atmospheric moisture.

Ti−MCM-41calc in the dehydrated form showed a very intense absorption peak in the preedge region at around 4970 eV assigned to the 1s → 3d transition, which is taken as a fingerprint of the presence of Ti in tetrahedral coordination.[13] However, the intensity of this band decreased upon exposure of the samples to atmospheric moisture, indicating that a large number of the Ti sites expand their coordination number from

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Table 2. Main Parameters of the Preedge Peaks of the Ti-Containing MCM-41 Catalysts Used in This Work

Ti−MCM-41 catalyst		peak position[a] (eV)	intensity[b]	fwhm (eV)
Ti−MCM-41calc	dehydrated	3.8	0.66	1.6
	hydrated	3.9	0.31	2.0
Ti−MCM-41sil	dehydrated	3.8	0.71	1.6
	hydrated	3.8	0.74	1.6

[a] Relative to the first inflection point of Ti metal (±0.2 eV). [b] Relative to the beginning of the EXAFS oscillations (±0.05).

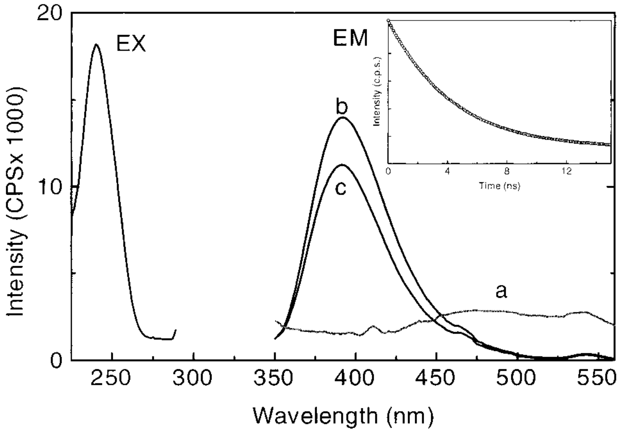

Figure 4. Emission spectra (EM) upon 250-nm excitation of Ti−MCM-41 recorded in quartz sealed cells after outgassing at 250 °C under 10^{-5} Torr for 2h: (a) Ti−MCM-41calc, (b) Ti−MCM-41sil. Spectrum c corresponds to the ambient-equilibrated Ti−MCM-41sil recorded without any outgassing treatment. EX corresponds to the excitation spectra monitoring the 390-nm emission for Ti−MCM-41sil. The inset shows the emission time profile monitored at 390 nm from Ti−MCM-41sil.

four to six. Distinctly, the silylated catalyst exhibited XANES spectrum that were very similar to that of the calcined catalyst upon dehydration, but it remained practically unaltered upon exposure to atmospheric humidity. These results clearly demonstrate that Ti sites located in the silylated mesoporous material do not interact with water molecules because of highly hydrophobic character of the Ti−MCM-41sil catalyst. The hydrophobicity of Ti−MCM41sil derives from the removal of OH groups through their transformation into $-OSi(CH_3)$ groups.

The preparation procedures and the spectroscopic characterization provide crucial information about the coordination number and the presence or absence of titanol groups necessary for understanding the remarkable differences in the fluorescence spectra of these samples. Thus, the luminescence of Ti−MCM-41calc after outgassing at 250 °C under reduced pressure of 10^{-5} Torr for 2h consisted of a weak, broad emission band (from 415 to 550 nm), as can be seen in Figure 4. Variation of the excitation wavelength from 225 to 280 nm does not alter the emission spectrum and only influences the relative emission intensity. The excitation spectrum for Ti−MCM-41calc essentially coincides with that shown in Figure 4 for Ti−MCM-41sil. According to the excitation spectrum, the maximum emission intensity is observed upon 235-nm excitation. In sharp contrast, the silylated sample exhibited, under the same conditions, a much more intense (about 2 orders of magnitude) emission that was remarkably blue-shifted with respect to the previous reports on the luminescence of porous titanosilicates.

Because silylation was accomplished using hexamethyldisilazane in toluene at 120 °C, we were concerned that trace amounts of this aromatic solvent or any other aromatic compound left in the solid were responsible for the observed emission. This possibility could be safely disregarded on the basis of the fact that purely siliceous MCM-41 submitted to exactly the same silylating treatment as that followed for Ti−MCM-41sil does not exhibit any measurable emission. If toluene or any other aromatic impurity were responsible for the emission of Ti−MCM-41sil, then they should be equally present in the MCM-41sil control sample but this was found not to be the case.

Taking into account the lack of titanol groups, an assignment of this unprecedented strong emission of Ti−MCM-41sil that would be compatible with the rest of characterization techniques is to Ti fluorophores in “closed” tetrapodal framework positions. Interestingly, the original Ti−MCM-41 sample before calcination and with channels full of template agent exhibits the same emission spectra with very similar intensity as the silylated samples. The fact that the 390-nm emission band has not been previously observed is likely due to differences in the preparation procedure and the nature of the Ti sites of the Ti−MCM-41 samples. Notably, calcination of Ti−MCM-41 results in the complete disappearance of the 390-nm band, indicating a dramatic and extensive change in the Ti atom coordination sphere. This would be compatible with partial $\equiv$Ti−O−Si $\equiv$ bond cleavage and the generation of $\equiv$Ti−OH titanol groups during this process. Subsequent silylation of these titanol groups in Ti−MCM-41sil will “restore” Ti atoms to the original $Ti-(OSi\equiv)_4$ coordination. These structural variations will be reflected also in the intensity of the emission, which was notably much higher for $Ti-(OSi\equiv)_4$ than for $\equiv$Ti−OH. Other alternative explanations, such as the presence of $\equiv Ti-O^-$ ions (counterbalanced by positive quaternary ammonium cations) being responsible for the 390-nm emission band in the original Ti−MCM-41, cannot be ruled out.

Again, in contrast to previous reports, one remarkable observation is that the 390-nm emission intensity of Ti−MCM-41sil is rather insensitive to the outgassing procedure (see Figure 4). This suggests that coadsorbed water and/or atmospheric oxygen cannot access the emissive species. Similar observations have been previously interpreted as an indication that the emissive Ti atoms are buried in the silicate framework, this being compatible with our assignment that the lumophores are not bipodal or tripodal Ti(OH) groups.

One point worth addressing is the fact that the wavelength corresponding to the maximum emission intensity is considerably blue-shifted with respect to the findings of previous reports on photoluminescence of micro- and mesoporous titanosilicates. Thus, we sought support that other titanium-containing molecules also emit in the region observed here (λ_{max} = 390 nm). In the literature, it has been reported that nanometric colloidal TiO_2 particles emit at 360 nm, although λ_{max} shifts progressively to longer wavelengths as the par-

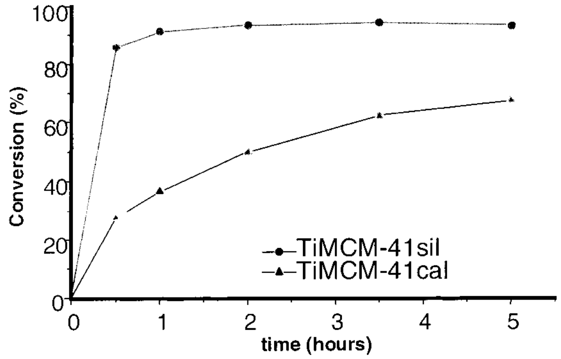

Figure 5. Activity of Ti−MCM-41calc and Ti−MCM-41sil as catalysts (300 mg) for the epoxidation of cyclohexene (16 mmol) with *tert*-butylhydroperoxide (4 mmol) at 60 °C.

ticles age.[14] Blue emission ($\lambda_{\max} = 390$ nm) of organic−TiO_2 hybrid particles has also been reported.[15] Furthermore, we also performed our own measurements with other control samples. Thus, we found that commercial titanium tetraisopropoxide has two weak fluorescent bands at ~340 and ~520 nm. Even more, samples of Ti−MCM-48, model titanosilsesquioxanes,[16] and TiO_2 clusters included in Y zeolites[17] all show emission below 400 nm. Definitely, molecules or materials containing Ti do exhibit emission below 400 nm. However, it should be recognized that the different electronic density on the oxygen atoms of the Ti−O lumophores of these models compared to that of the Ti−O−Si groups of siliceous matrixes could strongly influence the emission maximum of the luminescence spectra.

Surprisingly, no information about the kinetics of the emission of titanosilicates has yet been reported. Herein, we have determined that the emission of Ti−MCM-41sil decays on the nanosecond time scale (inset of Figure 4). This decay monitored at 390 nm can be adequately fit to the sum of two first-order decays, thus suggesting a distribution of luminescent Ti atoms in at least two families. These time-resolved studies open the possibility of monitoring the interaction of Ti atoms with quenchers.

The unprecendent fluorescence data can be correlated with the catalytic behavior of the these samples. Thus, silylation notably increased the catalytic performance of Ti−MCM-41calc for cyclohexene epoxidation using *tert*-butylhydroperoxide as the oxidant (Figure 5). The initial reaction rate for cyclohexene epoxidation was over 3 times higher. Therefore, the appearance of a 390-nm emission band related to the presence of tetrapodal framework Ti atoms could be taken as a sign of high catalytic activity.

In summary, on the basis of ^{29}Si-MAS NMR and XANES characterization, we propose that the unprecedented 390-nm band observed in the emission spectra of mesoporous titanosilicates is related to the presence of tetrapodal framework $Ti(OSi\equiv)_4$ lumophores. This is in clear contrast with previously reported results.[5−8] Additional work is in progress to study in detail the luminescence and emission kinetics of titanosilsesquioxanes as soluble model compounds as well as to investigate related Ti−MCM-48 catalysts to understand the Ti atom distribution observed by luminescence spectroscopy.

Experimental Section

Ti−MCM-41 materials were prepared using amorphous silica (Aerosil 200, from Degussa), 25 wt % solution of tretramethylammonium hydroxide (TMAOH, from Aldrich) as the basic source, and cetyltrimethylammonium bromide (CTAB, from Aldrich) as the liquid crystal templating agent. The Ti source was titanium tetraethoxide (TEOT, from Alpha Products). The gel composition for synthesizing the Ti−MCM-41was as follows:

$$SiO_2{:}(0.02\ TEOT){:}(0.26\ TMAOH){:}(0.12\ CTAB){:}(24\ H_2O)$$

The reaction mixture was autoclaved at 135 °C for 24 h; then, the as-prepared Ti−MCM-41 was collected by filtration, and the solid was washed and dried at 60 °C overnight. The as-prepared material was heated in a flow of dry N_2 at 540 °C for 1 h, and then subjected to a 6-h treatment in air flow at the same temperature to obtain the Ti−MCM-41calc.c sample.

Ti−MCM-41sil was obtained by silylation of Ti−MCM-41calc as follows: A 1-g sample of calcined Ti−MCM-41 was outgassed at 300 °C for 2 h. Then, 10 g of a solution containing the appropriate amount of hexamethyldisilazane (HMDS, obtained from ABCR GmbH & Co.) to give a HMDS/SiO_2 ratio equal to 0.12. Dry toluene was added under Ar onto the dehydrated Ti−MCM-41calc. The resulting mixture was refluxed under inert atmosphere at 120 °C for 2 h. After this time, the silylated Ti−MCM-4sil sample was filtered and thoroughly washed with 250 mL of toluene.

Diffuse reflectance UV−vis spectra were collected on Cary 5-G Varian spectrophotometer equipped with a "Praying Mantis" attachment from Harric and with $BaSO_4$ used as the reference. The X-ray absorption data for Ti−MCM-41 samples were collected using the synchrotron radiation provided by the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France) on the D21 line at the XAS2 station. The X-ray beam was emitted by the DCI storage ring running at 1.85 GeV with an average current of about 250 mA. X-ray radiation was monochromated using a Si(311) two-crystal monochromator. The Ti K-edge spectra were recorded at room temperature in fluorescence-yield mode using an eight-element Canberra detector. Samples were preheated under vacuum using suitable in situ cells, which allows for thermal treatment and measurement without contact of the sample with the atmosphere. XAS experimental data were analyzed using the XFIT v1.1 program.[18]

Emission and excitation spectra were obtained in an Edinburgh FS-900 spectrophotometer using a front-face attachment for solid samples. The powders were placed in Suprasil quartz cells and evacuated at 250 °C under 10^{-5} Torr for 2 h. After this time, the cells were sealed under vacuum. Lifetimes were measured with a FL-900 single-photon-counting photometer using a nanosecond hydrogen flash lamp.

The catalytic activity of the calcined and silylated Ti−MCM-41 materials was tested in epoxidation of cyclohexene using tertbutylhydroperoxide (TBHP) as the oxidant. In a typical catalytic run, 56 mmol of olefin was mixed with 14 mmol of TBHP (olefin/TBHP ratio = 4) at the reaction temperature of 60 °C. Then, 300 mg of catalyst (5 wt % catalyst) were added to the reaction medium. This instant was taken as time zero, and aliquots of the reaction media were withdrawn at different reaction times and subsequently analyzed by gas chromatography using a 5% phenylsilicone column (HP-5) of 25-m length.

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