

Surface UV/Vis Spectroscopy

The Usefulness of Time-Dependent Density Functional Theory to Describe the Electronic Spectra of Ti-Containing Catalysts**

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Several Ti-containing catalysts, including TS-1,^[1] Ti- β ,^[2] Ti-containing ordered mesoporous silica,^[3] amorphous xerogels,^[4] and Ti-supported silica,^[5] have exhibited a remarkably high efficiency and molecular selectivity in oxidation reactions with H₂O₂ under mild conditions. As a result of their relevance in industrial applications, they have been widely studied in recent years by several techniques, such as diffuse-reflectance spectroscopy coupled with UV/Vis spectroscopy

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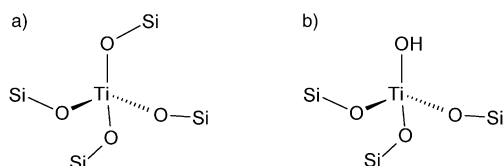
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(DRS-UV/Vis),^[6] X-ray absorption spectroscopy,^[7] and computer modeling studies.^[8]

Although there is currently a general agreement that the active site is a titanium center with tetrahedral coordination, there is still a considerable debate over the type of species present in the catalysts. The two widely accepted models are shown in Scheme 1. The stability of the species has been examined using computer modeling methods, and these suggest that the two species could be interconverted relatively easily by hydrolysis. Both species have been postulated to be present based on UV/Vis and photoluminescence experiments.^[6]



Scheme 1. Proposed models of tetrahedral Ti sites in dehydrated titanium catalysts: a) tetrapodal and b) tripodal.

One of the most useful tools to study the titanium environment is UV/Vis spectroscopy. The electronic spectra show an absorption associated with the ligand to metal charge transfer (LMCT) from the oxygen atom to the Ti^{IV} ion, namely $\text{Ti}^{4+}\text{O}^{2-} \rightarrow \text{Ti}^{3+}\text{O}^-$. The wavelength at which this transition occurs is highly sensitive to the coordination at the titanium sites, and this peculiarity has been proposed as a probe to test the coordination environment around a titanium center.^[6]

However, to our knowledge no studies aimed at correlating UV/Vis absorption with the photophysical properties calculated using time-dependent density functional theory (TD-DFT) has been reported. Thus, the two structures depicted in Scheme 1 have been studied. Tetrakis(trimethylsiloxy)titanium and titanosilicalite (TS-1) was selected as examples of the tetrapodal structure (Scheme 1 a), whereas a titanium-grafted amorphous silica substrate was taken as a model of the tripodal structure (Scheme 1 b). The initial geometry of the cluster selected for DFT calculations was taken from the literature^[7,8] and then the geometry fully optimized (see the Supporting Information). As already stated in an earlier study,^[9] the silicon atoms are terminated with hydrogen atoms. The geometry corresponds to that determined with experimental X-ray absorption fine structure (XAFS) data.^[7] Differences could be observed in the Si-O-Ti bond angles between the two models: the crystalline structure imposes a constrained geometry to the tetrapodal system, while the amorphous model has a more relaxed geometry. A good correlation between the experimental UV/Vis spectra and the electronic transitions derived from the TD-DFT analysis was found (Figures 1, 2, and 3).

The region of the electronic transitions calculated by TD-DFT on the tetrapodal model tetrakis(trimethylsiloxy)titanium (Figure 1) shows a sharp band centered at 214 nm, which is in excellent agreement with the spectrum determined experimentally. Good agreement is also observed between

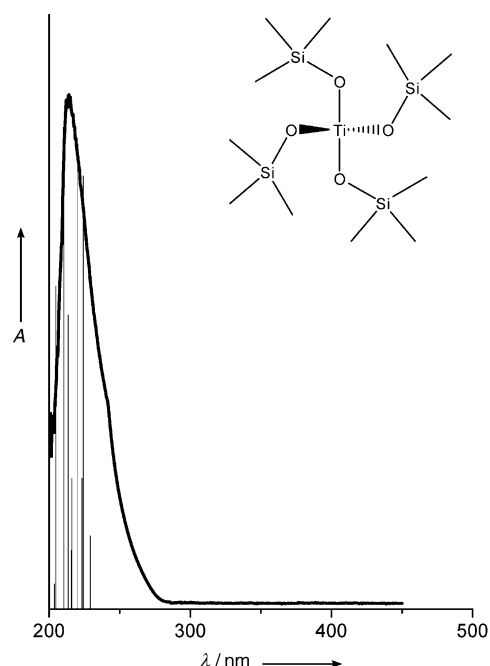


Figure 1. Experimental UV/Vis spectra and calculated transitions (bars) of tetrakis(trimethylsiloxy)titanium diluted in cyclohexane (10^{-5} M).

the calculated and experimental spectra of TS-1 (Figure 2 a). This finding indicates clearly that the major species present in TS-1 dried at high temperature (773 K) is the tetrapodal form. The electronic transitions of the tripodal system calculated by TD-DFT give rise to a broader band which is simultaneously shifted towards a greater wavelength (225 nm). These findings are in agreement with experimental observations (Figure 3 a) and with other results previously reported by other researchers using titanium-grafted mesoporous MCM-41 systems.^[6c]

The introduction of water molecules within the coordination sphere of the titanium cluster leads to a shift of the electronic transition calculated by TD-DFT to a greater wavelength (Figures 2 b and 3 b). This finding agrees with the experimental observation that an increase in the coordination number of the titanium center causes the wavelength of the LMCT transition to shift. It can be noted that the experimental spectrum of the TS-1 sample exhibits an absorption centered at 215 nm, with a shoulder at 250 nm (Figure 2 b), whereas that of the Ti/SiO_2 sample shows a shift of the peak to approximately 250 nm (Figure 3 b). As previously suggested by other researchers,^[6] this difference in the experimental spectra can be explained in terms of the different nature of TS-1 and Ti/SiO_2 substrates. The surface of TS-1 is hydrophobic by nature, which strongly hinders the access of molecular water to the titanium center. As a consequence, the number of titanium centers coordinated with water molecules are significantly reduced and a simultaneous decrease in the intensity of the signal at 250 nm occurs. However, since the silica surface is hydrophilic, the coordination of water molecules on surface Ti^{IV} centers is favored. It is emphasized here that the electronic spectrum of TS-1 with adsorbed water calculated by TD-DFT virtually coincided with that of Ti/SiO_2 . Since the selected cluster for TS-1 does

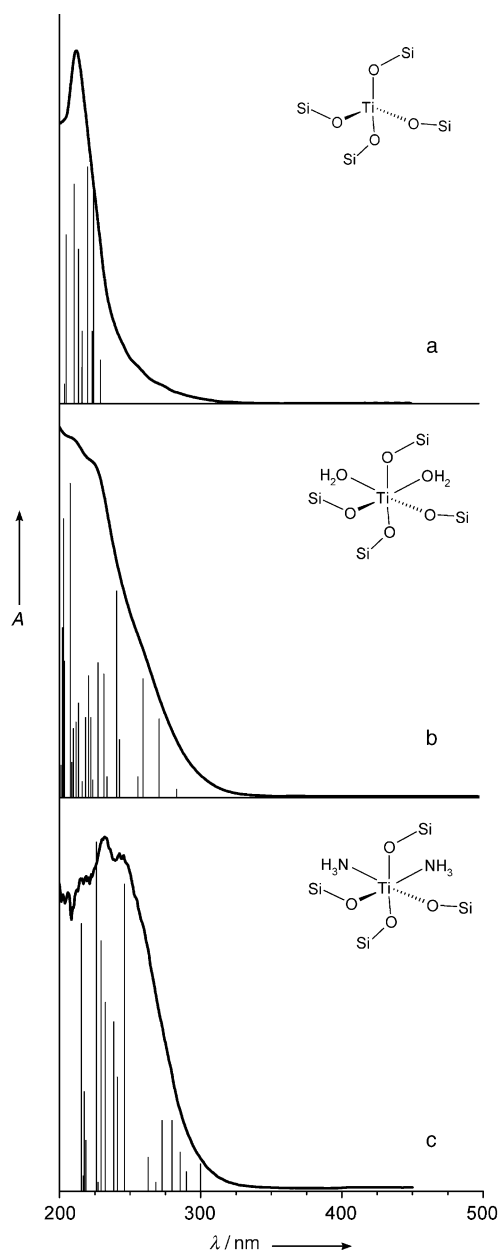


Figure 2. Experimental UV/Vis spectra and calculated transitions (bars) of TS-1: a) dried, b) exposed to water, and c) exposed to ammonia.

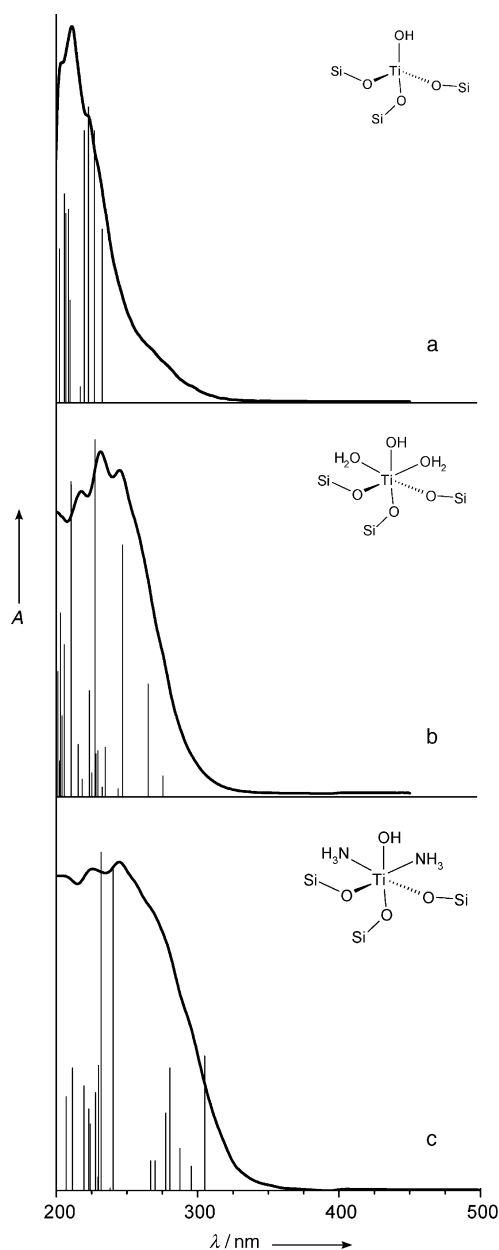


Figure 3. Experimental UV/Vis spectra and calculated transitions (bars) of Ti/SiO₂: a) dried, b) exposed to water, and c) exposed to ammonia.

not account for the hydrophobic character of the TS-1 channels, it is concluded that the presence of transitions at lower wavelength arise from LCMT transitions at Ti^{IV} centers with high coordination number as a result of coordinated water.

Similarly to the above, TD-DFT calculations were performed on the titanium cluster with coordinating ammonia molecules. In this case, the ammonia molecules entering the coordination sphere of the titanium cluster leads to a greater shift in the wavelength of the band relative to that observed with adsorbed water (Figure 2c and Figure 3c). Such a larger shift comes from the more basic character of ammonia molecules. This result is consistent with the experimental

spectra of both samples, which mirror the shift of the LMCT toward a longer wavelength. In accord with the adsorption of water molecules, no changes in the electronic spectra of the tetrapodal and tripodal structures were observed.

In conclusion, the photophysical properties of the titanium clusters were calculated using time-dependent density functional theory (TD-DFT)^[10] with a double zeta basis set (6-31G**). The electronic spectra of titanium-containing tetrapodal (TS-1) and tripodal (Ti/SiO₂) structures have been successfully described by time-dependent density functional theory (TD-DFT). The electronic transitions of the tetrapodal model calculated by TD-DFT gives a band centered at 216 nm, which is in excellent agreement with the experimen-

tal UV/Vis spectrum of TS-1. Similar TD-DFT calculations on the tripodal structure predicted a broader band which is shifted to a longer wavelength (225 nm). This prediction agrees with the experimental spectrum (Figure 3a) and with results previously reported on titanium-grafted mesoporous MCM-41 systems.^[6c] These TD-DFT calculations were also extended to the two titanium clusters into which either water or ammonia adsorbates were incorporated. In both cases a shift of the TD-DFT-calculated LMCT electronic transition to greater wavelength was predicted, thus showing clear differences between tetrahedrally and octahedrally coordinated Ti sites. This shift was larger with ammonia than with water because of the more basic character of ammonia molecules.

Experimental Section

A sample of TS-1 (1.5 Ti wt %) was synthesized following a literature procedure.^[1a] The supported titanium catalyst was prepared as described in the literature.^[5c]

UV/Vis transmission spectra were recorded on a solution of tetrakis(trimethylsiloxy)titanium (10^{-5} M) in cyclohexane with a Shimadzu UV-2401PC spectrometer. DRS-UV/Vis spectra were recorded with the same spectrometer to which an integrating sphere was incorporated. Solvent or pure BaSO₄ was taken as a reference. DRS-UV/Vis spectra were recorded from samples degassed under high vacuum at 773 K. Degassed samples were exposed to an excess of water or ammonia (25 mbar) and the gas phase was removed by degassing the solution at room temperature for 15 minutes.

Calculations were performed with the Gaussian 98 A.10. version suite of programs.^[11] Photophysical properties were calculated using TD-DFT.^[10] The validity of this theory for transition-metal ions has been checked by several authors.^[12] The gradient-corrected density functional methodology was employed: Becke's exchange functional (B)^[13] and Becke's three-parameter adiabatic connection (B3) hybrid^[14] exchange functional were used in combination with the Lee–Yang–Parr correlation functional.^[15] In all cases, the standard 6–31G** basis set of DZP (double-zeta + polarization) quality was used for orbital expansion to solve the Kohn–Sham equations.

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