

## Identifying Framework Titanium in TS-1 Zeolite by UV Resonance Raman Spectroscopy

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Framework titanium in Ti-silicalite-1 (TS-1) zeolite was selectively identified by its resonance Raman bands using ultraviolet (UV) Raman spectroscopy. Raman spectra of the TS-1 and silicalite-1 zeolites were obtained and compared using continuous wave laser lines at 244, 325, and 488 nm as the excitation sources. It was only with the excitation at 244 nm that resonance enhanced Raman bands at 490, 530, and 1125  $\text{cm}^{-1}$  appeared exclusively for the TS-1 zeolite. Furthermore, these bands increased in intensity with the crystallization time of the TS-1 zeolite. The Raman bands at 490, 530, and 1125  $\text{cm}^{-1}$  are identified as the framework titanium species because they only appeared when the laser excites the charge-transfer transition of the framework titanium species in the TS-1. No resonance Raman enhancement was detected for the bands of silicalite-1 zeolite and for the band at 960  $\text{cm}^{-1}$  of TS-1 with any of the excitation sources ranging from the visible to UV regions. This approach can be applicable for the identification of other transition metal ions substituted in the framework of a zeolite or any other molecular sieve.

## Introduction

The titanium-substituted silicalite-1, TS-1, zeolite with a MFI structure was first prepared by Tarahasso and colleagues<sup>1</sup> in 1983. TS-1 zeolite has received great interest during the past decade because of its excellent catalytic properties in a range of selective oxidation reactions with aqueous hydrogen peroxide (30%  $\text{H}_2\text{O}_2$ ) as the oxidant under mild conditions.<sup>2–6</sup> It is commonly believed that isolated titanium in the framework of the TS-1 zeolite, hereafter denoted as Ti–O–Si in this paper, is the active site for the selective oxidation although the exact nature of the active site is still in dispute.<sup>7</sup> There has been extensive characterization of TS-1 zeolite using the following techniques: FT-IR and Raman spectroscopy,<sup>4,5,8–17</sup> UV–visible absorption,<sup>10,12,13,17,18</sup> NMR,<sup>13,19–21</sup> EXAFS and XANES,<sup>15,16,22,23</sup> ESR,<sup>19</sup> XRD<sup>14,24</sup> ab initio,<sup>25</sup> and so on. A band at 960  $\text{cm}^{-1}$  appearing in Raman and IR spectra was assumed to be the characteristic vibration mode of the framework titanium species, Ti–O–Si. However, this band sometimes appears for silicalite zeolites without substituted titanium or with substituted metal instead of titanium and there is also evidence indicating that this band may be from surface hydroxyl (e.g., Si–OH)<sup>26,27</sup> or defect sites.<sup>28</sup> Thus, the key question still remains on how the framework titanium species can be identified unambiguously.

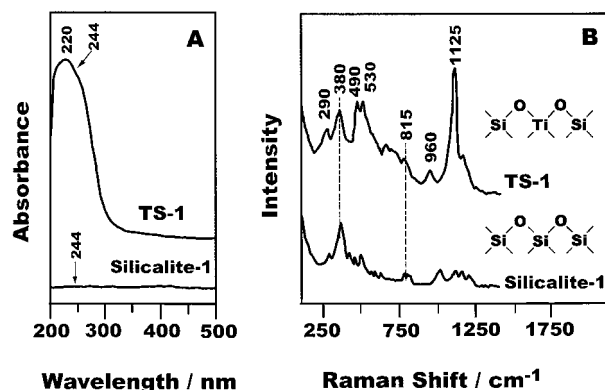
This study, using ultraviolet resonance Raman spectroscopy,<sup>29,30</sup> presents the first data that clearly distinguish the framework titanium from framework silicon and nonframework titanium dioxide. It makes use of the resonance Raman effect to selectively enhance the Raman bands associated with the framework titanium while keeping the rest of the Raman bands unchanged. The enhanced Raman bands can be directly associated with the framework titanium species Ti–O–Si in the zeolite because the excitation line approaches the charge-transfer absorption of framework Ti–O–Si species in the UV region (200–250 nm). In addition, the Raman spectrum with the

excitation lines in the UV region gives better signal-to-noise ratio than in the visible region, mainly because UV Raman spectroscopy can avoid most of the fluorescence interference from zeolite samples.<sup>30,31</sup> Therefore, UV resonance Raman spectroscopy is a potentially powerful technique to characterize the framework titanium in TS-1. This study also demonstrates that the UV resonance Raman spectroscopy is a general technique which can identify other transition-metals substituted in the framework of a zeolite or molecular sieves, based on the resonance Raman enhancement when there is an absorption due to the charge-transfer transition between the framework metal cations and oxygen anions.<sup>32,33</sup>

## Experimental Section

The continuous wave UV laser sources are from a Coherent Innova 300 Fred cw UV laser equipped with an intracavity frequency-doubling system using a BBO crystal to produce SHG(Second Harmonic Generation) outputs at different wavelengths, 229, 238, 244, 257, and 264 nm. 244 and 257 nm are the strongest lines and their power could be over 100 mw. A line at 325 nm is from a He–Cd laser with an output of 25 mW. A visible line at 488 nm from an Ar<sup>+</sup> laser(Spex Physics) is also used to obtain the normal Raman spectra. A spectrograph system was set up with an UV-sensitive CCD (Spex) and a triplemate (1877D, Jobin Yvon-Spex). Ti-silicalite-1(TS-1) and silicalite-1 zeolites were prepared according to the procedures reported by the ENI patent,<sup>1</sup> and the prepared zeolites were examined by XRD, UV–visible diffuse reflectance spectroscopy, FT–Raman spectroscopy, and FT–IR spectroscopy. XRD patterns show that the sample has a perfect MFI structure for TS-1 indirectly indicating the incorporation of some titanium ions in the framework of silicalite. The amount of titanium in the TS-1 was estimated to be less than 2% of the silicon atoms by ICP analysis. A band at 960  $\text{cm}^{-1}$ , similar to that observed in the literature, is also detected for our TS-1 sample by FT-Raman and FT-IR spectroscopy. These results confirm that the

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**Figure 1.** (A) UV-visible diffuse reflectance spectra of TS-1 and silicalite-1. (B) UV resonance Raman spectra of TS-1 and silicalite-1 excited with the 244 nm line.

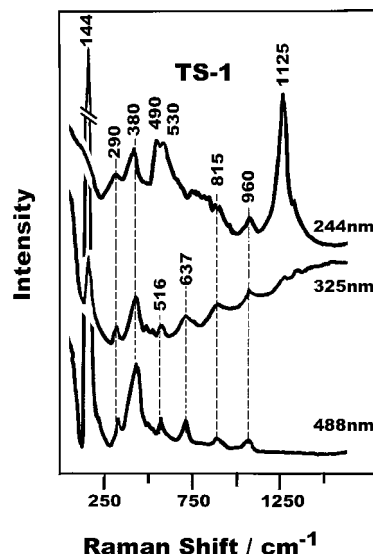
as prepared samples have the structures of TS-1 and silicalite zeolites.

## Results

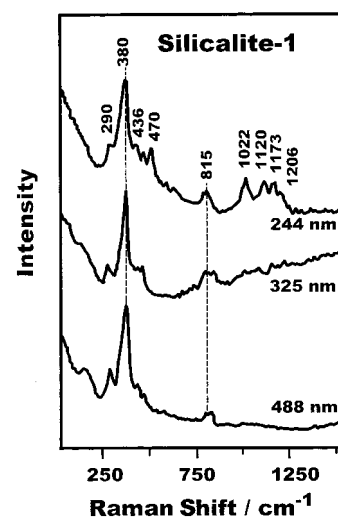
UV-visible diffuse reflectance spectra of TS-1 and silicalite (Figure 1A) show that there is a typical absorption band centered at 220 nm for TS-1 while no electronic absorption band is observed for silicalite-1. The band at 220 nm originates from the charge transfer of the  $p\pi$ - $d\pi$  transition between titanium and oxygen of the framework titanium species, Ti-O-Si, in the zeolite.<sup>10,18</sup> This transition involves the excitation of an electron from a  $\pi$  bonding molecular orbital consisting essentially of oxygen atomic orbital to a molecular orbital that is essentially a titanium atomic orbital. The tail of the band centered at 220 nm actually extends to 300 nm due to the presence of extraframework titanium species,  $TiO_2$ , in the TS-1 zeolite.

Figure 1B shows the UV Raman spectra of TS-1 and silicalite-1 excited by the 244 nm line. There are rich Raman bands observed for TS-1 at 1170 (shoulder), 1125, 960, 530, 490, 380, and 290  $cm^{-1}$  and some weak bands in the 600–800  $cm^{-1}$  region. Of particular interest is that a very strong band at 1125  $cm^{-1}$  is observed for TS-1 although usually the bands in the 1000  $cm^{-1}$  region are difficult to detect with normal Raman spectroscopy. The UV Raman spectrum of silicalite-1 is completely different from that of TS-1. The strong Raman bands at 490, 530, and 1125  $cm^{-1}$ , which appear for TS-1 are, absent, in the Raman spectrum of silicalite-1. These new bands at 490, 530, and 1125  $cm^{-1}$  must be from the framework titanium species in TS-1. Several common bands are observed at 290, 380, and 815  $cm^{-1}$  for both TS-1 and silicalite-1 zeolites indicating that these bands are the characteristics of silicalite-1 zeolite. The weak band at 960  $cm^{-1}$  in the UV Raman spectrum appears at the same frequency as in FT-IR and FT-Raman spectra.

Figure 2 exhibits the Raman spectra of TS-1 excited respectively by three different laser lines at 244, 325, and 488 nm. The strong bands at 490, 530, and 1125  $cm^{-1}$  are observed only when excited with the line at 244 nm. Clearly these bands are due to the UV resonance Raman effect because the 244 nm is in the absorbance band of the electronic absorption of TS-1 while the 325 and 488 nm lines are outside of the absorption band of TS-1 (Figure 1A). All three spectra have common bands at 290, 380, 815, and 960  $cm^{-1}$ , suggesting that these bands are not due to the resonance Raman effect but are the characteristics of silicalite-1 as shown in Figure 1B.



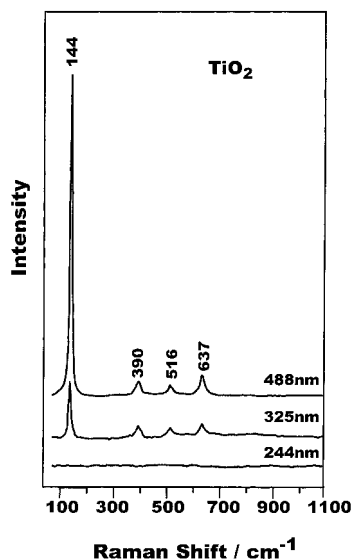
**Figure 2.** Raman spectra of TS-1 excited with laser lines at 244, 325, and 488 nm respectively.



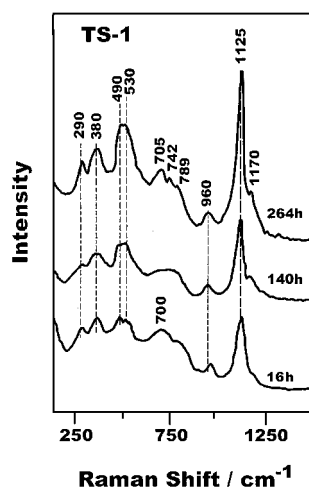
**Figure 3.** Raman spectra of silicalite-1 excited with laser lines at 244, 325, and 488 nm respectively.

In the Raman spectra of TS-1 excited at 325 and 488 nm, three additional bands at 144, 390, and 637  $cm^{-1}$  are observed. These bands are readily attributed to  $TiO_2$  (anatase) (see Figure 4), indicating that there are extraframework titanium species in the TS-1 sample. However, these bands are absent in the UV Raman spectrum from the excitation at 244 nm. It appears that visible Raman spectroscopy is sensitive to extraframework titanium species,  $TiO_2$ , while UV Raman spectroscopy is exclusively sensitive to the framework titanium species, Ti-O-Si.

The Raman spectra of silicalite-1 excited with lines at 244, 325, and 488 nm are almost identical (Figure 3). The interesting bands at 490, 530, and 1125  $cm^{-1}$  are not detected for silicalite-1 for excitation lines from the visible to ultraviolet regions. There is no resonance Raman phenomenon observed for silicalite-1 as no enhanced Raman bands are detected for silicalite-1 when the excitation line varied from the visible to the UV regions. This is in good agreement with the UV-visible diffuse reflectance spectrum in Figure 1A where there is no electronic absorption band for silicalite-1. Thus, it is confirmed that the bands at 490, 530, and 1125  $cm^{-1}$  are solely associated with the framework titanium of TS-1 but not with silicalite-1.



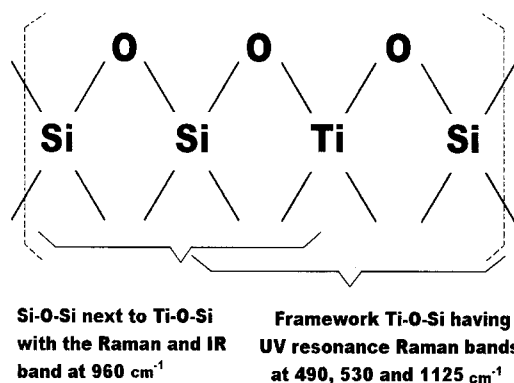
**Figure 4.** Raman spectra of  $\text{TiO}_2$  excited with 244, 325, and 488 nm respectively.



**Figure 5.** UV resonance Raman spectra of TS-1 excited with 244 nm for different crystallization time.

The Raman bands at 290, 380, and 815  $\text{cm}^{-1}$  do not vary with the different excitation lines at 244, 325, and 488 nm indicating that these bands are the characteristic bands of silicalite-1 itself. Especially, the band at 380  $\text{cm}^{-1}$  is the identification of the MFI structure.<sup>8</sup> These bands also appear for TS-1 suggesting that TS-1 still keep the main structure of silicalite-1. There are some weak bands in the 1000–1200  $\text{cm}^{-1}$  region which are also due to silicalite-1. These bands become evident when the excitation is shifted from 488 to 244 nm mainly due to less fluorescence interference in the Raman spectrum when the excitation wavelength is shifted from the visible to the ultraviolet regions.

The resonance enhanced Raman bands at 490, 530, and 1125  $\text{cm}^{-1}$  can be attributed to framework titanium species in tetrahedral coordination as depicted in Figure 6. These vibrational modes can be assigned simply from the analysis of the local unit of a  $[\text{Ti}(\text{OSi})_4]$ , denoted as Ti–O–Si in this paper. The bands at 490 and 530  $\text{cm}^{-1}$  are respectively assigned to the bending and symmetric stretching vibrations of the framework Ti–O–Si species and the band at 1125  $\text{cm}^{-1}$  is attributed to the asymmetric stretching vibration of the Ti–O–Si.<sup>8,10</sup> The band at 1125  $\text{cm}^{-1}$  is most enhanced in the UV resonance Raman spectrum because this vibration mode is more sensitive to the charge-transfer transition of Ti–O–Si.



**Figure 6.** Assignment of the UV resonance Raman bands at 490, 530, and 1125  $\text{cm}^{-1}$ , and the commonly observed IR and Raman band at 960  $\text{cm}^{-1}$ .

The Raman spectra of  $\text{TiO}_2$  excited with 244, 325, and 488 nm are shown in Figure 4. There are four bands at 144, 390, 516, and 637  $\text{cm}^{-1}$  due to  $\text{TiO}_2$ (anatase) in the visible Raman spectrum(excitation at 488 nm). These bands appear exactly at the same positions as with the excitation at 325 nm, but the intensities of these bands decrease dramatically. Very interestingly, these bands are almost absent in the Raman spectrum from the excitation at 244 nm. This phenomenon can be explained in terms of nonradiation and fluorescence processes in the  $\text{TiO}_2$  when excited with UV light.  $\text{TiO}_2$  strongly absorbs UV (244 nm) light because  $\text{TiO}_2$  has a broad band ranging from 200 to 350 nm. The absorbed light becomes mainly nonradiation and fluorescence<sup>34,35</sup> because there is a strong fluorescence band in the 380–420 nm region. Consequently, the fraction of Raman radiation is very small, and it is hard to detect the UV Raman bands of  $\text{TiO}_2$  from an excitation in its solid energy band. Another reason is that the small portion of UV Raman scattering present is re-adsorbed before escaping from the sample. The Raman signal can still be seen with the excitation at 325 nm because the 325 nm line is off the center of the absorption band of  $\text{TiO}_2$  and its Raman scattering can partly escape from the sample. However, these Raman signals are much weaker than those with the excitation at 488 nm because 325 nm is still on the tail of the UV–visible absorption band of  $\text{TiO}_2$ .

To rule out the possibility that nanoparticles of  $\text{TiO}_2$  in the zeolite may give the resonance Raman band, a nanoparticle powder of  $\text{TiO}_2$  with sizes from 1 to 10 nm was also characterized by UV Raman spectroscopy with the excitation at 244 nm. No detectable Raman bands were observed for the nanoparticle  $\text{TiO}_2$  in the UV Raman spectra. Therefore, the enhanced Raman bands observed at 490, 530, and 1125  $\text{cm}^{-1}$  for TS-1 are solely from the framework Ti–O–Si species.

The bands at 144, 390, 516, and 637  $\text{cm}^{-1}$  due to  $\text{TiO}_2$  predominate the Raman spectra of TS-1 with the excitations at 325 and 488 nm in Figure 2 and Figure 4. It is straightforward to deduce that a certain quantity of  $\text{TiO}_2$  exists in TS-1 as the extraframework titanium species. This is well in accordance with the UV–visible absorption result (Figure 1A). It seems that extraframework titanium species is always produced as a byproduct accompanying the synthesis of the TS-1 zeolite. However, Raman bands of  $\text{TiO}_2$  are not detected either for TS-1 or  $\text{TiO}_2$  in the UV Raman spectrum with excitation at 244 nm. This suggests that the UV resonance Raman spectroscopy is able to selectively identify the framework titanium species Ti–O–Si in TS-1 irrespective of the existence of the extraframework titanium species,  $\text{TiO}_2$ .

The evolution of the framework titanium species in TS-1 was followed by UV resonance Raman spectroscopy during the



crystallization of the zeolite as shown in Figure 5. The relative intensities of the resonance Raman bands at 490, 530, and 1125  $\text{cm}^{-1}$  significantly increased with the crystallization time, while the other bands, for example, 290, 370, and 960  $\text{cm}^{-1}$ , are only slightly changed. In addition, these resonance Raman bands, particularly the band at 1125  $\text{cm}^{-1}$  become narrower for longer crystallization time indicating that the framework titanium becomes more uniform in the TS-1. The fact that the bands at 490, 530, and 1125  $\text{cm}^{-1}$  develop with crystallization time strongly suggests that more framework titanium species are derived and/or the structure of the framework titanium becomes more compatible with the silicalite-1 structure. The relative intensities of the resonance bands at 490, 530, and 1125  $\text{cm}^{-1}$  can be an estimation of how much framework titanium species is incorporated in the silicalite-1 structure and how well the crystal structure of TS-1 is formed.

## Discussion

Prior to this work, the framework titanium in TS-1 was characterized mainly by the band at 960  $\text{cm}^{-1}$  when using FT-IR and normal Raman spectroscopy (with the excitations at 488, 514, or 1064 nm). It was assumed that the appearance of the band at 960  $\text{cm}^{-1}$  is the indication that framework titanium is formed in the TS-1. However, the assignment of this band has been controversial so far, e.g., this band was also assigned to titanyl group  $\text{Ti}=\text{O}$ ,<sup>8,36</sup>  $\text{Ti}-\text{O}$  stretching, silanol group  $\text{Si}-\text{OH}$ , titanium related defect sites,<sup>10</sup>  $\text{Ti}-\text{O}-\text{Si}$  bridge<sup>8</sup> and among others. This band is detected for TS-1 in this study by UV Raman and visible Raman spectroscopy (see Figures 1 and 2), and also by FT-Raman spectroscopy. But the relative intensity of this band is almost the same with the different excitation lines (Figure 2). This clearly means that the band is not a resonance-related Raman band. In other words, this band is not directly associated with the framework titanium species in TS-1 because the resonance phenomenon originates from the charge-transfer transition between titanium cations and oxygen anions in the framework of TS-1. The fact that the relative intensity of the band at 960  $\text{cm}^{-1}$  remains almost unchanged with the crystallization time (Figure 5) again suggests that the band at 960  $\text{cm}^{-1}$  is not associated with the framework titanium species of TS-1. It is concluded from these results that the band at 960  $\text{cm}^{-1}$  is only indirectly associated with the framework titanium. Most possibly it is from the  $\text{Si}-\text{O}-\text{Si}$  species next to the framework  $\text{Ti}-\text{O}-\text{Si}$  species as described in Figure 6.

There are some vibrational modes in the 960  $\text{cm}^{-1}$  region due to the vibration of  $\text{Si}-\text{O}-\text{Si}$  in silicalite-1 zeolite, but these bands are extremely weak in both the IR spectrum and the Raman spectrum mainly due to symmetry limitations. When a foreign atom (e.g., Ti or any other metals, such as V, Fe, etc.) is introduced into the framework of silicalite-1, the local symmetry of the  $\text{Si}-\text{O}-\text{Si}$  next to the foreign atom is slightly distorted and the vibrational band of  $\text{Si}-\text{O}-\text{Si}$  becomes infrared and Raman active. This is why silicalite zeolite substituted with other transition metals instead of titanium also shows the band at 960  $\text{cm}^{-1}$ . This reasoning also explains how sometimes a weak band at 960  $\text{cm}^{-1}$  is observed even for a pure silicalite without any substituted transition metals because any defect or hydroxyl in the zeolite may induce the symmetry distortion of the  $\text{Si}-\text{O}-\text{Si}$ . The band at 960  $\text{cm}^{-1}$  did not grow with an increase of the framework titanium<sup>37</sup> because the symmetric distortion effect of the framework titanium on the  $\text{Si}-\text{O}-\text{Si}$  may cancel each other when the concentration of titanium in the framework is increased. Therefore, the appearance of the band at 960  $\text{cm}^{-1}$  is not a reliable indication of the formation of framework titanium species in the TS-1.

The maximum amount of framework titanium in TS-1 was estimated to be no more than 3% of silicon atoms. The amount of framework titanium in our TS-1 sample is less than 2% because the total content of titanium is about 2%. Certainly, framework titanium in such low concentration is hard to detect or to discriminate by usual spectroscopic techniques. It is the resonance Raman effect that makes it possible for the sensitive and selective identification of the framework titanium species,  $\text{Ti}-\text{O}-\text{Si}$ , in TS-1 because the resonance between electronic and vibrational states can make the resonance Raman intensity several orders of magnitude stronger than a normal Raman band.

## Conclusions

Three resonance enhanced Raman bands at 490, 530, and 1125  $\text{cm}^{-1}$  are observed exclusively for TS-1 zeolite in the UV resonance Raman spectra. These bands are the characteristics of the framework titanium species in TS-1 zeolite because these bands appear only when UV laser (244 nm) excites the charge transfer transition of the framework titanium species in the TS-1 zeolite. The framework titanium in TS-1 can be successfully identified by the UV resonance Raman spectroscopy. It is also shown that the band at 960  $\text{cm}^{-1}$  is not directly associated with framework titanium  $\text{Ti}-\text{O}-\text{Si}$  but with  $\text{Si}-\text{O}-\text{Si}$  near the framework titanium species or any other defect site. The UV resonance Raman spectroscopy of this report also opens up the possibility of identifying the other transition metal cations incorporated into the framework of a zeolite or other molecular sieves.

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