

# Raman Spectroscopy of Vanadium Oxide Species Immobilized at Surface Titanium Centers of Mesoporous Titanosilicate TiMCM-41 Molecular Sieves

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The vanadium oxide species immobilized at surface titanium centers of mesoporous titanosilicate TiMCM-41 molecular sieves have been studied by Raman spectroscopy to establish a better structural understanding of these vanadium oxide species and their transformations. Siliceous MCM-41 gives a Raman spectrum similar to that of amorphous SiO<sub>2</sub> except that a band at 978 cm<sup>-1</sup> from surface silanol groups is much more intense. This supports a previous finding that the amorphous silica walls of MCM-41 contain abundant silanol groups. Incorporation of titanium into the MCM-41 framework dramatically reduces the Raman intensity due to strong fluorescence and reduction of the local symmetry arising from a longer Ti–O bond relative to a Si–O bond. Vanadium oxide supported on siliceous MCM-41 in its calcined form shows an intense Raman band at 1033 cm<sup>-1</sup> characteristic of terminal vanadyl groups. This suggests that V<sup>5+</sup> is present in siliceous MCM-41 as an isolated tetrahedral vanadate species possessing one normal terminal V=O bond and three V–O–Si bonds to the support. In contrast, such a Raman band is not observed in vanadium oxide supported on TiMCM-41 with low vanadium loading. This is suggested to be due to the affinity of titanium for oxygen to produce a stronger Ti–O bond than a Si–O bond and thus a stretched terminal V=O bond. As the vanadium loading on TiMCM-41 increases beyond a critical V/Ti ratio of 0.33, a broad feature in the 800–900 cm<sup>-1</sup> region is resolved and assigned to bridged V–O–V chain vibrations of polymeric vanadium oxide species. This feature shifts to higher frequency as the vanadium loading increases. Simultaneously, the 1033 cm<sup>-1</sup> band observed in vanadium oxide supported on siliceous MCM-41 appears, indicating additional bonding between vanadium species and titanium-free surface sites. Prolonged laser illumination of samples with high vanadium loading results in the disappearance of the broad feature in the 800–900 cm<sup>-1</sup> region as well as a band near 960 cm<sup>-1</sup> together with an intensity increase in the band at 1033 cm<sup>-1</sup>. This indicates that surface dehydration and dehydroxylation occur under laser illumination together with decomposition of the polymeric vanadium oxide species immobilized at titanium centers which migrate to titanium-free surface sites.

## Introduction

Supported vanadium oxides consisting of a surface monolayer dispersed on a high surface area oxide support such as TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, or SiO<sub>2</sub> have been used as commercial catalysts for the selective catalytic reduction of NO and NO<sub>2</sub> (NO<sub>x</sub>) by ammonia in the presence of O<sub>2</sub> for two decades.<sup>1–3</sup> These materials also exhibit promising catalytic properties toward a number of industrially important selective oxidations of hydrocarbons, such as *o*-xylene to phthalic anhydride<sup>4,5</sup> and toluene to benzaldehyde or benzoic acid.<sup>6,7</sup> Activity and selectivity studies have demonstrated that TiO<sub>2</sub> is the most successful support.<sup>7,8</sup> Spectroscopic characterizations have revealed that at low surface coverage (<1 wt % V<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub>) the surface vanadium oxide species is present as an isolated tetrahedral vanadate species, which possesses one terminal V=O bond and three V–O bonds to the support, while at higher surface coverage polymeric tetrahedral metavanadates usually appear.<sup>9–13</sup> The molecular structures of these vanadium oxide species are generally dependent on the surface vanadium oxide coverage and on the extent of surface hydration, but not directly on the specific oxide support.<sup>8,10</sup> The dramatic promotion effect of the TiO<sub>2</sub> support on the catalytic performance of surface vanadium oxide species is considered to be due to the stronger redox characteristics of TiO<sub>2</sub> compared to those of other oxide supports.<sup>8</sup> This led to a suggestion that the bridging V–O bonds

to the support play a more important role than the terminal V=O bond in these selective oxidation reactions.<sup>8</sup>

TiO<sub>2</sub> normally possesses a moderate surface area of about 50 m<sup>2</sup>/g.<sup>11b</sup> Attention has been paid to developing TiO<sub>2</sub> supports with higher surface areas up to 200 m<sup>2</sup>/g to support larger amounts of active vanadium species and to allow faster diffusion of both reactants and products to potentially improve catalytic performance.<sup>14</sup> Related to this issue, Mobil's scientists have made an important breakthrough.<sup>15</sup> They have prepared mesoporous siliceous MCM-41 molecular sieve which possess uniform channels of about 30 Å in diameter with a large internal surface area up to 1000 m<sup>2</sup>/g<sup>16</sup> and have used it as a support for titanium and vanadium oxides via a two-step impregnation procedure.<sup>15</sup> The resultant material exhibits comparable selective catalytic reduction reactivity of NO<sub>x</sub> to a commercial WO<sub>3</sub>–V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst. However, the molecular picture of the structure of the supported titanium–vanadium mixed oxide species on MCM-41 remains unclear.

Most recently we reported some progress toward this goal.<sup>17</sup> In contrast to Mobil's work, our strategy is to use a titanium-substituted mesoporous TiMCM-41 molecular sieve to support vanadium oxide species. Our previous electron spin resonance (ESR) and diffuse reflectance ultraviolet–visible (UV–vis) spectroscopic studies have revealed that the surface titanium centers immobilize the vanadium species and promote the oxidation of VO<sup>2+</sup> to V<sup>5+</sup> due to a strong interaction between the vanadium oxide species and the surface titanium centers. The spectroscopic data support the postulate that the surface

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vanadium oxide species is four-coordinated at low vanadium loading. Since the surface coverage of vanadium oxide over the titanium centers can be adjusted by controlling either the 4-fold-coordinated titanium content or the vanadium loading and since four-coordinated titanium is more active than six-coordinated titanium,<sup>18</sup> better V–O bonding to the support occurs. This material may have advantages compared to conventionally prepared  $V_2O_5/TiO_2$  catalysts.

Direct structural measurements of the vanadium oxide phase supported on TiMCM-41 can be carried out in principle by solid-state  $^{51}V$  NMR.<sup>12</sup> However, our  $^{51}V$  NMR measurements have shown poor spectroscopic resolution probably due to the low vanadium loading on these MCM-41 materials. In the present investigation we employ Raman spectroscopy to discriminate between surface vanadium oxide species. A molecular structural scheme of surface vanadium oxide species and their transformations upon incipient-wetness impregnation, calcination, and rehydration is proposed.

## Experimental Section

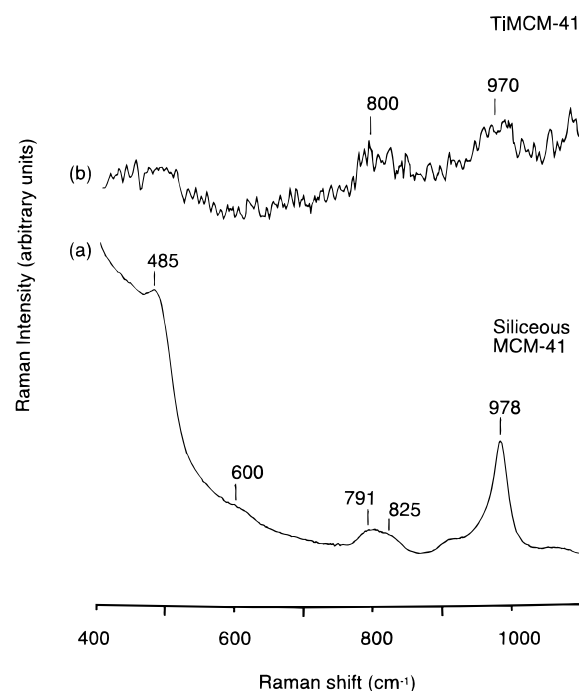
**Sample Preparation.** Siliceous MCM-41 and TiMCM-41 with a Si/Ti ratio of 17 were synthesized according to the literature<sup>19</sup> and used as vanadium oxide supports. The detailed procedure for vanadium loading by incipient-wetness impregnation has been described.<sup>17</sup> These samples were calcined in static air at 550 °C for 24 h prior to laser Raman measurement.

**Raman Spectroscopy.** The Raman spectra were acquired on 1 cm diameter round solid pellets of the samples at room temperature. The samples were positioned in a 135° front scattering geometry.<sup>20</sup> The laser line used was 406.7 nm (violet) from a Coherent K-2 CW krypton ion laser to minimize the fluorescence background seen in many of the samples. The laser power was set between 70 and 150 mW depending on the amount of fluorescence seen in the samples. A Spex 1403 double monochromator, equipped with 1800 grooves/mm holographic gratings and a Hamamatsu 928 photomultiplier detection system, was used to record all the spectra under control of a Spex DM3000 microcomputer system.<sup>21</sup> The Raman data were obtained at 2  $cm^{-1}$  increments over the 400–1100  $cm^{-1}$  range with monochromator slit settings to give a spectral band-pass of 2–4  $cm^{-1}$ . Multiple scans (10–30) were averaged to improve the signal-to-noise ratio. For cases where strong background scattering from the TiMCM-41 support made analysis difficult, a representative sloping linear baseline was subtracted from the spectrum.

## Results

**Support Materials.** It is first necessary to assign the vibrations arising from siliceous MCM-41 and TiMCM-41 to isolate the vibrations associated with surface vanadium oxide species. Figure 1a shows the Raman spectrum of siliceous MCM-41 which exhibits spectroscopic features similar to amorphous  $SiO_2$  except that the line at 978  $cm^{-1}$  is more intense in MCM-41. Based on previous literature assignments for silicate materials,<sup>11b,12b</sup> the bands at 791 and 825  $cm^{-1}$  are assigned to siloxane linkages (Si–O–Si) and the bands at 485 and 600  $cm^{-1}$  to three Si and four Si siloxane rings. The 978  $cm^{-1}$  band in siliceous MCM-41 can only be assigned to surface silanol ( $O_3Si-OH$ ) stretching vibrations because of its purely siliceous composition. This is consistent with a previous assignment of a weak band in the 980–990  $cm^{-1}$  region for amorphous  $SiO_2$  (Cab-O-Sil).<sup>12b,22</sup>

Previous Raman and infrared spectroscopic characterizations of various titanium-substituted silicalites revealed that a band at around 960  $cm^{-1}$  appears upon substitution of titanium into

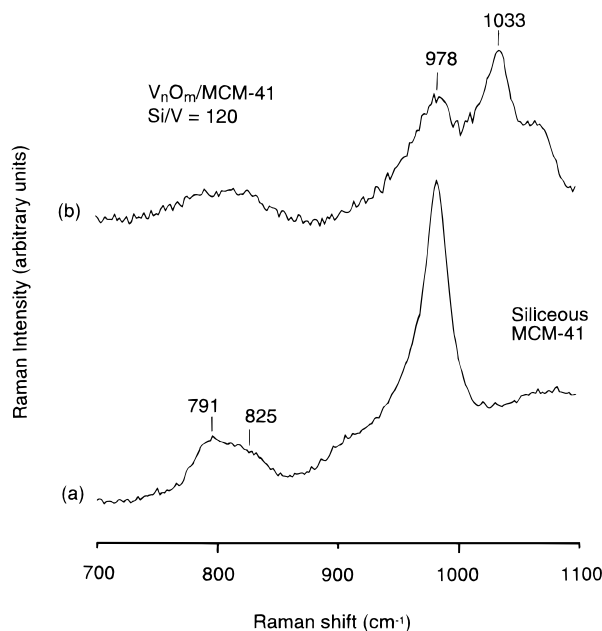


**Figure 1.** Raman spectra at 293 K of (a) siliceous MCM-41 and (b) TiMCM-41. A sloping linear background over the 400–1100  $cm^{-1}$  region has been subtracted in (b).

a silicalite framework.<sup>18</sup> Since crystalline siliceous microporous molecular sieves are essentially featureless in this range and the integrated intensity of the 960  $cm^{-1}$  band increases linearly with the titanium amount, this band has been assigned to antisymmetric Ti–O–Si stretching modes of corner-sharing tetrahedra.<sup>18</sup> But the origin and interpretation of this band are controversial,<sup>22</sup> and this assignment is questionable as titanium-free siliceous MCM-41 gives a more prominent band near this position both in infrared spectra reported previously<sup>23,24</sup> and in the Raman spectrum at 978  $cm^{-1}$  in this work. Since  $^{29}Si$  MAS NMR spectroscopy has demonstrated that about 20% of the silicons in siliceous MCM-41 are  $Si(OSi)_3OH$  units which dominate the  $^{29}Si$  MAS NMR spectrum under  $^1H-^{29}Si$  cross-polarization conditions,<sup>25</sup> our assignment of this intense 978  $cm^{-1}$  band to terminal silanol groups on the siliceous MCM-41 wall surfaces seems convincing.

In contrast to siliceous MCM-41, TiMCM-41 gives a very weak Raman spectrum shown in Figure 1b. The large background is largely due to fluorescence. Very weak broad Raman features at 450  $cm^{-1}$  (siloxane rings), 800  $cm^{-1}$  (siloxane bridges), and 970  $cm^{-1}$  (terminal silanol groups) are assigned by comparison with MCM-41. Since the weak spectrum only occurs after siliceous MCM-41 has titanium incorporated, it can be interpreted that the Ti–O bonds are longer than the Si–O bonds,<sup>18</sup> and thus the incorporation of titanium into the second coordination sphere of framework silicons destroys the symmetry of the silicon tetrahedra on which the Raman intensity depends. On the other hand, the  $TiO_2$  particles are known to have strong Raman scattering properties, and their presence is readily detected by intense Raman bands at 400, 530, and 640  $cm^{-1}$ .<sup>26</sup> All of these bands are absent in the Raman spectrum of TiMCM-41; thus, the formation of the  $TiO_2$  phase in TiMCM-41 during crystallization or upon calcination can be ruled out. This is consistent with a framework location of titanium in TiMCM-41 revealed previously by X-ray absorption<sup>19</sup> and UV–vis spectroscopies.<sup>17</sup>

**Vanadium Oxide Supported on Siliceous MCM-41.** Figure 2b shows the Raman spectrum of vanadium oxide supported

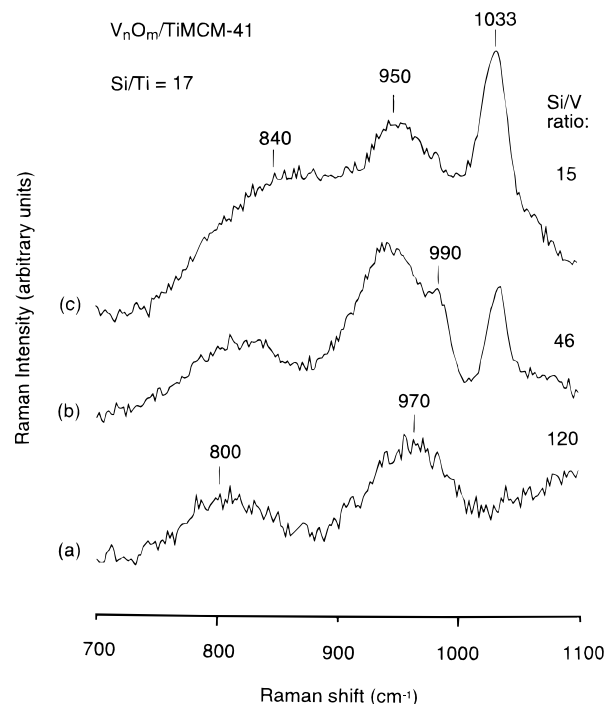


**Figure 2.** Raman spectra at 293 K of (a) siliceous MCM-41 and (b) vanadium oxide supported on siliceous MCM-41.

on siliceous MCM-41. As compared to siliceous MCM-41 (Figure 2a), it exhibits a reduced 978 cm<sup>-1</sup> band intensity and an additional strong band at 1033 cm<sup>-1</sup>. Because the position of the band at 1033 cm<sup>-1</sup> is similar to that observed for vanadium oxytrihalides (OVX<sub>3</sub>, X = F, Cl, Br) and such a band has been assigned for supported V<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, or SiO<sub>2</sub> to an isolated vanadyl species possessing one terminal V=O bond and three bridging V—O—support bonds on the basis of <sup>51</sup>V NMR, Raman, infrared, and phosphorescence spectroscopies,<sup>8,11,12</sup> the 1033 cm<sup>-1</sup> band is similarly assigned here. The reduced intensity of the 978 cm<sup>-1</sup> band with vanadium loading suggests that monomeric vanadium species occupy wall surface silanol sites.

**Vanadium Oxide Supported on TiMCM-41.** Figure 3 shows the Raman spectra of vanadium oxides supported on TiMCM-41 at different vanadium loadings. At low vanadium loading the Raman spectrum does not show any new features different from TiMCM-41 (Figure 3a, Figure 1b). In contrast to vanadium oxide supported on siliceous MCM-41, the band at 1033 cm<sup>-1</sup> due to monomeric vanadyl species does not appear (Figure 3a, Figure 2b). The reason for this difference is probably related to how the vanadium oxide binds to the support. Since our previous ESR and UV-vis studies have shown that V—O bonds to four-coordinated titanium centers in TiMCM-41 more strongly than it does to siliceous MCM-41 surfaces,<sup>17</sup> we suggest that the absence of the Raman V=O band at 1033 cm<sup>-1</sup> for vanadium oxide species supported on TiMCM-41 is due to a stretched terminal V=O bond in V—O—Ti compared to V—O—Si and that this stretched V=O bond is less Raman-active.

With increasing vanadium oxide loading on TiMCM-41 to a Si/V ratio of 46 for a Si/Ti ratio of 17, which corresponds to a V/Ti ratio of 0.37 above the critical V/Ti ratio of about 0.33,<sup>17</sup> the Raman band at 1033 cm<sup>-1</sup> due to monomeric vanadyl species becomes resolvable and another broad band around 990 cm<sup>-1</sup> develops (Figure 3b). The 990 cm<sup>-1</sup> band is similar to the band associated with terminal V=O bands in polymeric tetrahedral metavanadates<sup>11b</sup> to which it is assigned. This suggests that additional coordination of a monomeric vanadyl species to a surface siliceous site occurs after all exposed surface titanium centers are occupied by vanadyl species and that these

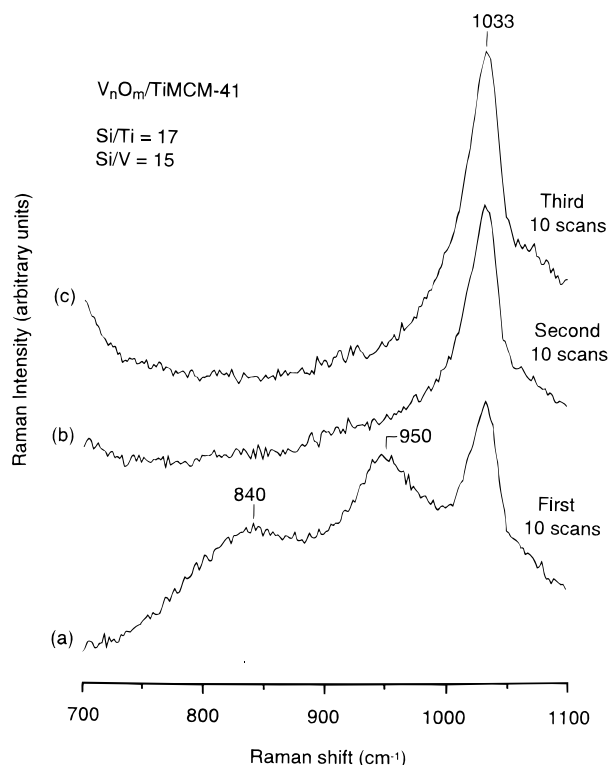


**Figure 3.** Raman spectra at 293 K of vanadium oxide supported on TiMCM-41 with Si/V ratios of (a) 120, (b) 46, and (c) 15. The spectra are displayed following subtraction of a sloping linear background over the 700–1100 cm<sup>-1</sup> region.

“overloaded” vanadyl species prefer a location near the titanium centers. This is consistent with previous ESR and UV-vis results.<sup>17</sup>

At higher vanadium loading to a Si/V ratio of 15, the 1033 cm<sup>-1</sup> band due to monomeric vanadyl species increases in intensity. In addition, a new broad feature at 800–900 cm<sup>-1</sup> appears and shifts to higher frequency with increasing vanadium loading. The Raman band near 840 cm<sup>-1</sup> seems characteristic of V—O—V bending vibrations in polyvanadate species which have a band at 810 cm<sup>-1</sup> for [HV<sub>2</sub>O<sub>7</sub>]<sup>3-</sup> and a higher frequency band at 840 cm<sup>-1</sup> for [V<sub>10</sub>O<sub>28</sub>]<sup>6-</sup> with increased molecular weight.<sup>11</sup> Therefore, the shift of this 800–900 cm<sup>-1</sup> Raman band to higher frequency as the vanadium oxide loading increases suggests an increase in the molecular weight of the polyvanadate species. In addition, these Raman bands do not match those of crystalline V<sub>2</sub>O<sub>5</sub>, which possesses sharp Raman bands at 994, 702, and 527 cm<sup>-1</sup>. Therefore, crystalline V<sub>2</sub>O<sub>5</sub> on TiMCM-41 at any level of vanadium loading does not seem to be present.

**Dispersion of Polymeric Vanadium Oxide under Laser Illumination.** The samples may experience laser-induced dehydration and/or dehydroxylation during acquisition of the Raman spectra.<sup>15,16</sup> To examine this effect, Raman spectra were recorded after various periods of laser illumination for a TiMCM-41 sample with high vanadium loading. As shown in Figure 4, with prolonged laser illumination bands at 840 cm<sup>-1</sup> due to vanadium clusters and at 950 cm<sup>-1</sup> due to surface terminal silanol groups decrease, while the 1033 cm<sup>-1</sup> band due to monomeric vanadyl species at siliceous sites increases. The laser beam apparently induces surface dehydration and dehydroxylation and promotes vanadium cluster decomposition and migration to siliceous surface sites. But it is curious that most Raman features contributed by the silicate framework disappear under prolonged laser illumination. This may be due to framework rearrangement. It is interesting to note that these effects of laser illumination on vanadium oxide supported on TiMCM-41 can be reversed by prolonged exposure to hydrated



**Figure 4.** Raman spectra at 293 K after prolonged laser illumination of vanadium oxide supported on TiMCM-41 with Si/V ratio of 15: (a) average of first 10 scans, (b) average of second 10 scans, and (c) average of third 10 scans. The spectra are displayed following subtraction of a sloping linear background over the 700–1100  $\text{cm}^{-1}$  region.

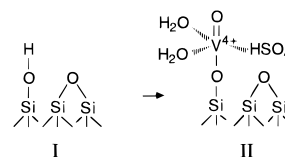
air at low vanadium loading, but not at high vanadium loading, which is consistent with ESR and UV–vis results.<sup>17</sup> However, following recalcination, all samples give Raman spectra identical with those prior to prolonged laser illumination.

## Discussion

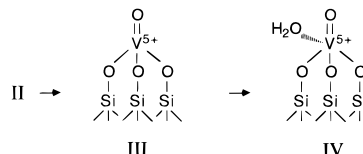
The Raman spectroscopic results agree generally with conclusions from previous ESR and UV–vis spectroscopic results.<sup>17</sup> The vanadium oxide is present as monomeric species at surface titanium centers of TiMCM-41 when the vanadium loading is low, and more than two vanadium oxide species may accumulate at a single titanium center when vanadium loading is high. The primary role of the titanium centers in TiMCM-41 is to control the distribution of the vanadium oxide species and, thereby, to affect their structure. In addition, Raman spectroscopy suggests that the monomeric vanadium oxide species immobilized at titanium centers of TiMCM-41 have stronger V–O bonds to the support and thus a stretched terminal V=O bond compared to siliceous MCM-41. This phenomenon is due to the strong oxygen affinity of titanium.<sup>27–29</sup> Based on these Raman spectroscopic observations along with previous ESR and UV–vis spectroscopic findings,<sup>17</sup> it is possible to suggest the following probable vanadium oxide structures and their transformations upon incipient-wetness impregnation, calcination, and rehydration.

**Siliceous MCM-41 Supported Vanadium Oxide.** Raman spectroscopy shows that siliceous MCM-41 wall surfaces possess abundant terminal silicon hydroxyls (Figure 5, structure I), which originate from electrostatic interaction between the cationic surfactant and silicate oligomers<sup>30</sup> and are finally formed following surfactant decomposition during calcination. Upon incipient-wetness impregnation of MCM-41 by vanadyl sulfate solution,  $\text{VO}^{2+}$  is suggested to react with a hydroxyl to form

Incipient-wetness impregnation:

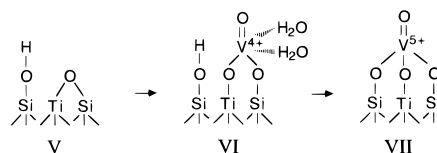


Calcination, and then rehydration:

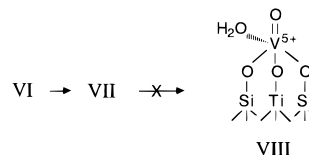


**Figure 5.** Schematic structural transformations proposed for vanadium oxide supported on siliceous MCM-41 upon incipient-wetness impregnation, calcination, and rehydration.

Incipient-wetness impregnation:



Calcination, and then rehydration:



**Figure 6.** Schematic structural transformations proposed for vanadium oxide supported on TiMCM-41 with low vanadium loading upon incipient-wetness impregnation, calcination, and rehydration.

structure II (Figure 5) with one weak V–O–Si bond. This vanadyl species can thus reorient rapidly to give an isotropic ESR signal as observed.<sup>17</sup> In addition, these vanadyl ions are relatively stable on siliceous MCM-41 and have the green color of  $\text{VO}^{2+}$  ions.

After calcination, vanadium is completely oxidized to  $\text{V}^{5+}$  and adopts tetrahedral geometry with one normal terminal V=O bond and three V–O–Si bonds (structure III in Figure 5). A similar structure has been suggested for vanadium oxides on  $\text{SiO}_2$  supports.<sup>11b</sup> This  $\text{V}^{5+}$  structure III has a white color, is ESR silent, and has a Raman band at 1033  $\text{cm}^{-1}$  and a UV–vis band of tetrahedral  $\text{V}^{5+}$  ions. Since the interaction between the vanadium oxide species and siliceous MCM-41 surfaces is weak, water molecules can enter the coordination sphere of the central  $\text{V}^{5+}$  ions to form five- and/or six-coordinated  $\text{V}^{5+}$  species (structure IV in Figure 5) as revealed by UV–vis and the corresponding color change from white to yellow.<sup>17</sup> The hydrated  $\text{V}^{5+}$  ions in structure IV give a more intense and better resolved Raman band at 1033  $\text{cm}^{-1}$  than in structure III, which is probably associated with a more symmetric environment for the central  $\text{V}^{5+}$  ions due to additional coordination with water ligands.

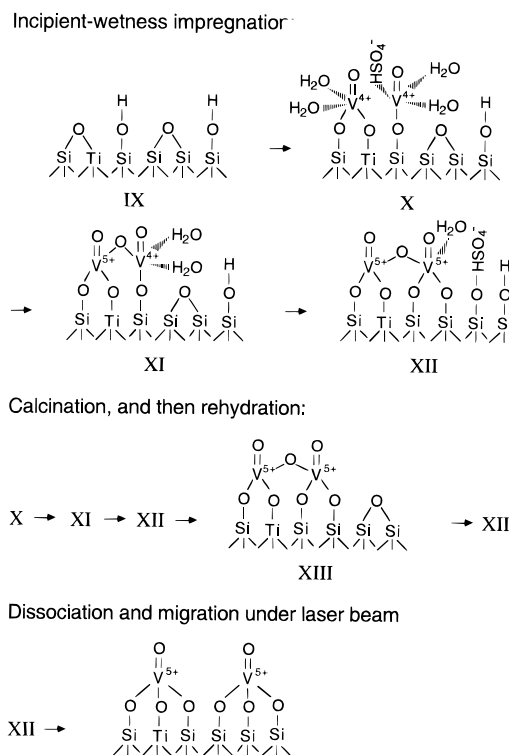
**TiMCM-41 Supported Vanadium Oxide with Low Vanadium Loading.** With four-coordinated titanium centers in TiMCM-41 (Figure 6, structure V), the hydrated vanadyl species in the incipient wetness solution is monatomically dispersed on surface titanium centers with one strong V–O–Ti bond and one or two V–O–Si bonds (structure VI in Figure 6). This structure gives an anisotropic ESR spectrum of  $\text{VO}^{2+}$  com-

plexes.<sup>17</sup> These  $\text{VO}^{2+}$  species on TiMCM-41 are unstable and can be readily oxidized to  $\text{V}^{5+}$  (structure **VII**) due to the strong reducibility of the titanium centers. This corresponds to a color change from green of  $\text{VO}^{2+}$  to white of tetrahedral  $\text{V}^{5+}$  ions and a decreased ESR intensity of  $\text{VO}^{2+}$  ions compared to siliceous MCM-41.<sup>17</sup> Structure **VII** consisting of one terminal  $\text{V}=\text{O}$  bond, one  $\text{V}-\text{O}-\text{Ti}$  bond, and two  $\text{V}-\text{O}-\text{Si}$  bonds is similar to structure **III** of vanadium oxide on siliceous MCM-41. However, the Raman spectral feature at  $1033\text{ cm}^{-1}$  attributed to the  $\text{V}=\text{O}$  stretch in structure **III** is absent in structure **VII**. Considering the closely analogous structures of **VII** and **III**, this difference deserves additional comment as follows.

Previous studies on  $\text{TiO}_2$  supported group VIII metal catalysts for CO hydrogenation have revealed that upon  $\text{H}_2$  reduction the  $\text{TiO}_2$  support exhibits a strong oxygen affinity for the oxygen end of CO which promotes CO disassociation and enhances the hydrogenation activity of the metal centers.<sup>27–29</sup> Titanium  $\text{Ni}_3\text{Ti}$  and  $\text{Pt}_3\text{Ti}$  alloy catalysts also exhibit oxygen affinity upon exposure to  $\text{O}_2$  or CO which induces titanium segregation over the alloy surface.<sup>31</sup> For vanadium oxide catalysts supported on  $\text{TiO}_2$  there is a dramatic promotion effect on the catalytic performance of the surface vanadium species while this does not occur on  $\text{SiO}_2$ .<sup>8</sup> This has been interpreted as due to the redox characteristics of  $\text{TiO}_2$  supports.<sup>8</sup> The titanium in these  $\text{TiO}_2$  supports is six-coordinated. Four-coordinated Ti as in titanium-substituted silicate-1 (TS-1) is even more active than six-coordinated titanium.<sup>18</sup>

TiMCM-41 also contains four-coordinated titanium centers which are active toward oxidation of large organic molecules.<sup>24</sup> Loading of vanadium oxides on TiMCM-41 gives an axially symmetric ESR signal characteristic of atomically dispersed  $\text{VO}^{2+}$  ions.<sup>17</sup> In addition, an immediate color change from blue to white with vanadium loading indicates rapid oxidation of vanadium from  $\text{VO}^{2+}$  to tetrahedral  $\text{V}^{5+}$  ions which is confirmed by UV–vis. In contrast, vanadium oxide loaded on siliceous MCM-41 gives an isotropic ESR signal typical of mobile  $\text{VO}^{2+}$  ions and shows a blue color. Upon calcination and hydration in moist air, these  $\text{VO}^{2+}$  ions are oxidized to  $\text{V}^{5+}$  ions and achieve a higher coordination number of five or six. Since these differences occur in going from siliceous MCM-41 to TiMCM-41, a reasonable interpretation is that there is a strong interaction between vanadium and surface titanium centers, as in  $\text{Ti}-\text{O}-\text{V}$ , which immobilizes the vanadium species and promotes the oxidation of  $\text{VO}^{2+}$  to  $\text{V}^{5+}$ . Consistent with these ESR and UV–vis observations and with previously reported vanadium oxide structures on  $\text{TiO}_2$ , we have proposed a possible vanadium oxide structure on TiMCM-41 which consists of one terminal  $\text{V}=\text{O}$  bond, one  $\text{V}-\text{O}$  titanium bond, and two  $\text{V}-\text{O}-\text{Si}$  bonds or  $(\text{Si}-\text{O})_2\text{V}=\text{O}(-\text{O}-\text{Ti})$  (structure **VII**).<sup>17</sup> However, in that work we did not detect a normal  $\text{V}=\text{O}$  stretch for structure **VII** which is present in siliceous MCM-41 (structure **III**). The Raman spectroscopic experiments show a striking difference between these two cases, which suggests that a  $\text{V}=\text{O}$  bond is modified by four-coordinated titaniums in TiMCM-41. The reasonable interpretation is that this  $\text{V}=\text{O}$  bond is stretched in  $\text{Ti}-\text{O}-\text{V}$ .

Calcination results in complete oxidation of  $\text{VO}^{2+}$  to  $\text{V}^{5+}$  ions (structure **VI** to structure **VII**) as indicated by the disappearance of the ESR signal of  $\text{VO}^{2+}$  and a color change from light-yellow to white.<sup>17</sup> In contrast to siliceous MCM-41, water molecules cannot enter the coordination sphere of the  $\text{V}^{5+}$  ions to form five- and/or six-coordinated  $\text{V}^{5+}$  species (structure **VIII**) because of the strong  $\text{V}-\text{O}-\text{Ti}$  linkage. Also due to the strong  $\text{V}-\text{O}-\text{Ti}$  linkage, Raman spectroscopy



**Figure 7.** Schematic structural transformations proposed for vanadium oxide supported on TiMCM-41 with high vanadium loading upon incipient-wetness impregnation, calcination, rehydration, and laser illumination.

suggests that the terminal  $\text{V}=\text{O}$  bond in structure **VII** is stretched and less Raman-active.

**TiMCM-41 Supported Vanadium Oxide with High Vanadium Loading.** Increasing vanadium oxide coverage on TiMCM-41 over the critical V/Ti ratio allows more than two  $\text{VO}^{2+}$  ions to compete for a single surface titanium center (Figure 7, structure **X**) and causes a broad ESR singlet without hyperfine structure.<sup>17</sup> For TiMCM-41 with low vanadium loading, these  $\text{VO}^{2+}$  species near titanium centers are unstable and can be gradually oxidized to  $\text{V}^{5+}$  (structures **XI** and **XII**) in air, corresponding to a color change from green of  $\text{VO}^{2+}$  to yellow of octahedral  $\text{V}^{5+}$  ions.<sup>17</sup> This process can be promoted by calcination to form tetrahedral surface  $\text{V}^{5+}$  clusters with a white color (structure **XIII**) as revealed by UV–vis and Raman spectroscopies. These vanadium clusters are still isolated at each titanium center of TiMCM-41, but their bond to the TiMCM-41 support is weaker than at low vanadium loading since water molecules can coordinate with the central  $\text{V}^{5+}$  ions as reflected by a reversible color change of white tetrahedral  $\text{V}^{5+}$  ions to yellow octahedral  $\text{V}^{5+}$  ions during repeated dehydration and hydration treatments.<sup>17</sup>

When such a sample is subjected to prolonged laser illumination, the TiMCM-41 surface may experience laser-induced dehydration and/or dehydroxylation. The vanadium clusters are decomposed, and the resulting monomers migrate to siliceous sites.

## Conclusions

Based on previous ESR and UV–vis characterization, laser Raman spectroscopy has been employed to study the molecular structures of vanadium oxide species immobilized at surface titanium centers of TiMCM-41 molecular sieves. Siliceous MCM-41 has amorphous  $\text{SiO}_2$  walls, and the wall surfaces possess terminal silicon hydroxyls indicated by an intense Raman band at  $978\text{ cm}^{-1}$ . Incorporation of titanium into the

MCM-41 framework destroys the symmetry of the silicon tetrahedras and dramatically reduces the intensity of this Raman signal. The vanadium oxide species on siliceous MCM-41 possess one normal terminal V=O bond and three V–O–Si bonds to the support and give an intense Raman band at 1033 cm<sup>-1</sup> characteristic of terminal vanadyl groups. The same structure is also suggested for vanadium oxide species on TiMCM-41 with low vanadium loading, but the terminal V=O bond is suggested to be stretched and Raman-inactive due to the stronger oxygen affinity of titanium. With increasing vanadium loading beyond the critical V/Ti ratio of about 0.33, the 1033 cm<sup>-1</sup> band becomes observable due to additional bonding between adjacent vanadium oxide species and titanium-free surface sites. In addition, polymeric vanadium oxide species also occur on TiMCM-41 as indicated by a broad feature in the 800–900 cm<sup>-1</sup> region. A TiMCM-41 sample with high vanadium loading experiences surface dehydration and dehydroxylation under prolonged laser illumination with simultaneous decomposition of the polymeric vanadium oxide species.

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