

Electron Spin Resonance and Diffuse Reflectance Ultraviolet–Visible Spectroscopies of Vanadium Immobilized at Surface Titanium Centers of Titanosilicate Mesoporous TiMCM-41 Molecular Sieves

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A series of mesoporous titanosilicate TiMCM-41 molecular sieves with variable amounts of framework titanium have been hydrothermally synthesized using H_2O_2 as a phase stabilizer. Some structurally analogous materials containing framework zirconium (ZrMCM-41), aluminum (AlMCM-41), or only silicon (MCM-41) have also been synthesized. These materials are calcined to decompose the organic structure-directing agent and used as vanadium supports. Vanadium is loaded onto the supports by incipient-wetness impregnation of a dilute (0.001–0.017 M) aqueous vanadyl sulfate solution. The chemical environment of vanadium in these materials is investigated by electron spin resonance and diffuse reflectance ultraviolet–visible spectroscopy. Both techniques reveal that in freshly prepared siliceous MCM-41 or AlMCM-41 with either low or high vanadium loading only mobile vanadyl VO^{2+} ions are detected. By contrast, in freshly prepared TiMCM-41 or ZrMCM-41 with low vanadium loading, vanadium exists as monatomically dispersed square-pyramidal VO^{2+} ions and tetrahedral V^{5+} ions. This indicates that surface titanium or zirconium centers immobilize these vanadium species and promote the oxidation of VO^{2+} to V^{5+} . Thus, a strong interaction between vanadium and surface titanium or zirconium centers is suggested. As the vanadium loading in TiMCM-41 increases beyond a critical V/Ti ratio of about 0.17, VO^{2+} clusters develop, and some square-pyramidal and distorted octahedral V^{5+} ions occur simultaneously by additional coordination to water molecules. This suggests that the accumulation of more than two vanadium ions at a single titanium center occurs at higher vanadium loading. Upon calcination and rehydration in moist air, vanadium is completely oxidized to tetrahedral V^{5+} when the vanadium loading is below a critical V/Ti ratio of 0.33 or to some square-pyramidal and octahedral V^{5+} at higher vanadium loading. Such an increase in the critical V/Ti ratio on calcination suggests that calcination gives rise to a greater dispersion of the surface vanadium species on the wall surfaces of TiMCM-41.

Introduction

Supported vanadium oxides consisting of a surface vanadium oxide phase on a high surface area oxide support such as TiO_2 , ZrO_2 , Al_2O_3 , or SiO_2 are widely used catalysts for selective oxidation reactions of hydrocarbons, such as *o*-xylene to phthalic anhydride^{1,2} and toluene to benzaldehyde or benzoic acid.^{3,4} This type of catalyst is also important for selective catalytic reduction (SCR) of NO_x by ammonia in the presence of O_2 and has become an established technique for the removal of nitrogen oxides.^{5–7} In the past decade considerable effort has been devoted to understanding the structure of these catalysts and their catalytic effect on reaction activity and selectivity.^{6–12} Attention has also been paid to developing oxide supports with higher surface area up to 200 m^2/g to immobilize larger amounts of active vanadium species.¹³

Activity and selectivity studies have demonstrated that the type of specific oxide support has a great influence on the surface molecular structure of the vanadium oxide and on its catalytic performance. By far, the most successful support for vanadium in these selective oxidation reactions is TiO_2 .^{4,14} For $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts^{7–9,13} both activity and selectivity increase with increasing vanadium loading up to a theoretical monolayer coverage of about 0.1 wt % V_2O_5 per square meter of TiO_2 surface.¹¹ This is attributed to the parallel increase of the surface concentration of the active vanadium species. Lower surface coverage of vanadium oxide generally results in poor reaction

selectivity since exposed TiO_2 sites lead to an undesired combustion of the partial oxidation products. At higher vanadium loading than a monolayer coverage both the activity and selectivity decrease.¹⁴ Obviously, such catalytic performance cannot be attributed to either pure V_2O_5 or pure TiO_2 ; thus, some modification of either or both components in the catalyst has been suggested.^{10,12}

Direct structural measurements of the vanadium oxide phase on these supports have been carried out mostly by x-ray absorption (EXAFS and XANES),^{15,16} by laser Raman,^{8,14,17} and recently by ^{51}V NMR.¹² In the $\text{V}_2\text{O}_5/\text{TiO}_2$ system these methods revealed a specific vanadium oxide–titanium oxide interaction in comparison with V_2O_5 being supported on SiO_2 or Al_2O_3 ¹¹ and that the structure of vanadium oxide phase is different from that of bulk V_2O_5 but with a two-dimensional vanadium oxide overlayer attached to the TiO_2 support.^{12,14} Two different surface vanadium oxide species are apparently present on the TiO_2 support. One is assigned to an isolated tetrahedral vanadate species possessing one terminal $\text{V}=\text{O}$ bond and three $\text{V}-\text{O}$ bonds to the support and usually dominates at low surface coverage (<1 wt % V_2O_5 on TiO_2). Another one is assigned to polymeric tetrahedral metavanadates which are essentially dioxo species and generally appear at higher surface coverage. These vanadium species are found to be the active sites in $\text{V}_2\text{O}_5/\text{TiO}_2$ for selective oxidation reactions. On other oxide supports essentially the same vanadium oxide species have been identified; however, these materials exhibit quite different reactivities.^{14,17} This dramatic promotion effect of the oxide support

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TABLE 1: Color and Elemental Composition of V/TiMCM-41, V/ZrMCM-41, V/AlMCM-41, and V/MCM-41

sample	composition		color		
	Si/Ti ratio ^a	Si/V ratio ^b	fresh-prepared	calcined	rehydrated
V/TiMCM-41-(10)	11	60	white	white	white
V/TiMCM-41-(20)	17	60	light yellow	white	light yellow
V/TiMCM-41-(40)	44	60	yellowish-green	white	yellow
V/TiMCM-41-(80)	81	60	green	white	orange
V/MCM-41		60	green	white	orange
V/AlMCM-41-(30)	47(Si/Al)	60	green	white	orange
V/ZrMCM-41-(20)		60	yellowish-green	white	yellow

^a By electron microprobe analysis or Si/Al where indicated. ^b From chemical stoichiometric composition in incipient-wetness impregnation.

on the catalytic performance of surface vanadium species is related to the redox characteristics of the pure oxide supports. This led to a suggestion that the bridging V–O bonds to the support, rather than the terminal V=O bond, are associated with the active sites for selective oxidation reactions.¹⁴

The TiO₂ support, in which titanium is 6-fold-coordinated, is predominantly used as a heterogeneous catalyst in photocatalytic processes.¹⁸ As titanium also exists as 4-fold-coordinated in silica framework sites, such as in titanium-substituted silicalite-1^{19,20} (TS-1), it exhibits remarkable catalytic properties toward the oxidation of a large family of organic molecules.²¹ TiMCM-41, as the first titanium-substituted mesoporous molecular sieve, also contains atomically dispersed titanium centers at 4-fold-coordinated silica framework sites.^{22,23} Like its siliceous MCM-41 analog,²⁴ TiMCM-41 synthesized using cetyltrimethylammonium chloride as a structure-directing agent possesses uniform mesopore channels of about 30 Å diameter with a large internal surface area up to 1000 m²/g.²² This makes it a suitable support for transition-metal oxides. In this work we prepare TiMCM-41 supported vanadium oxide, V/TiMCM-41. We expect that this material may have advantages compared to conventionally prepared V₂O₅/TiO₂ catalysts as follows. First, the surface coverage of vanadium over the titanium centers can be adjusted by controlling the 4-fold-coordinated titanium content and the vanadium loading. Second, the 4-fold-coordinated titanium and vanadium both are atomically dispersed in TiMCM-41, which may modify the V–O bonding to the support. Third, the large internal surface and pore size of TiMCM-41 allows fast diffusion of both reactants and products to potentially improve catalytic performance.

This work realizes the first approach toward this goal. TiMCM-41 is synthesized and used as a support to prepare V/TiMCM-41 by incipient-wetness impregnation. The same method is used to prepare other analogous materials with framework zirconium (V/ZrMCM-41), aluminum (V/AlMCM-41), and silicon (V/MCM-41). Electron spin resonance (ESR) and diffuse reflectance ultraviolet–visible spectroscopy (UV–vis) are employed to study the chemical environment of vanadium in these materials. The results show that in V/TiMCM-41 there exists a strong surface interaction between vanadium and the titanium centers and that titanium catalyzes the oxidation of VO²⁺ to V⁵⁺. The same phenomenon is observed in V/ZrMCM-41, but not in V/AlMCM-41 or V/MCM-41.

Experimental Section

Synthesis. TiMCM-41 with a variable Si/Ti ratio was synthesized using titanium(IV) ethoxide as the titanium source as described before.²³ Titanium ethoxide is dissolved in a mixture of water and hydrogen peroxide to form a clear orange solution before adding to the silica gel mixture. In this way, rapid hydrolysis of the titanium source and the precipitation of TiO₂ are prevented.²⁵ These samples are designated as TiMCM-41-(X), where X is the Si/Ti ratio in the gel. AlMCM-41 with

a Si/Al ratio of 30 in the gel, designated as AlMCM-41-(30), and siliceous MCM-41 were synthesized according to the literature.^{26a} The same procedure was applied to the synthesis of ZrMCM-41 with a Si/Zr ratio in the gel of 20 using zirconium(IV) ethoxide as the zirconium source. This sample is designated ZrMCM-41-(20). These samples are calcined in static air at 550 °C for 24 h to decompose the organic structure-directing agent. The final white solid powders are used as vanadium supports.

Impregnation. Vanadium was loaded onto the supports at room temperature by incipient-wetness impregnation with 6 times by weight of an aqueous vanadyl sulfate solution. The vanadium concentration in the aqueous vanadyl sulfate solution varies over 0.001–0.017 M.

Vanadium-impregnated samples are dried in air at room temperature in a shallow dish for 2 days. Calcination is performed in static air at 550 °C for 24 h. For thermal reduction, samples are evacuated to 10^{−4} Torr and heated to 200 °C for 1 h.

Characterization. The elemental composition of the resultant solid products was analyzed by an electron microprobe using a Jeol JXA-8600 spectrometer. The results are given in Table 1. Corresponding color changes of these samples upon vanadium loading and thermal treatment are also presented in Table 1.

Powder XRD patterns were collected before and after calcination using a Philips 1840 powder diffractometer with Cu Kα radiation (40 kV, 25 mA) with a 0.025° step size and 1 s step time over the range 1.5° < 2θ < 15°. The samples were prepared as thin layers on aluminum slides.

For ESR measurements, samples were loaded into 3 mm o.d. by 2 mm i.d. Suprasil quartz tubes. Room temperature ESR spectra were recorded at X-band on a Bruker ESP 300 spectrometer. The magnetic field was calibrated with a Varian E-500 gaussmeter. The microwave frequency was measured by a Hewlett-Packard 5342A frequency counter.

The diffuse reflectance UV–vis spectra were measured with a Perkin-Elmer 330 spectrophotometer equipped with a 60 mm Hitachi integrating sphere accessory. Powder samples were loaded in a quartz cell with Suprasil windows, and spectra were collected in the wavelength range 200–1000 nm against a siliceous MCM-41 standard.

Results

XRD and Composition Analysis. XRD patterns of TiMCM-41 with a Si/Ti ratio lower than 20 are shown in Figure 1. A well-resolved XRD pattern is obtained from TiMCM-41-(20) (Figure 1a), which is typical of siliceous MCM-41 materials.²⁴ After calcination to decompose the surfactant, its XRD pattern becomes better resolved (Figure 1a'), which is consistent with siliceous MCM-41.^{26a} As the Si/Ti ratio approaches 10, the (100) peak still shows good shape in XRD patterns of both as-synthesized and calcined materials, but the peaks at 2θ > 3° become less resolved (Figure 1b,b'). With further increase of

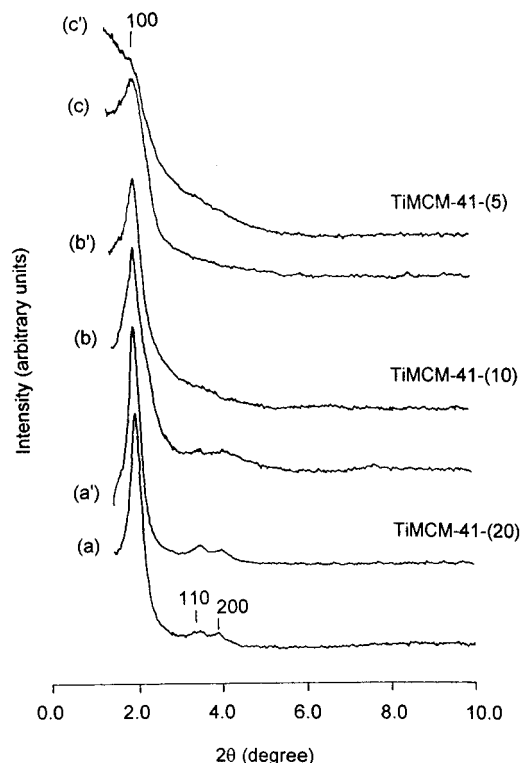


Figure 1. XRD patterns of as-synthesized TiMCM-41 samples: (a) TiMCM-41-(20), (b) TiMCM-41-(10), and (c) TiMCM-41-(5). (a'), (b'), and (c') are XRD patterns of corresponding calcined samples.

titanium content to a Si/Ti ratio of 5, the XRD pattern becomes very poorly resolved, especially after calcination (Figure 1c,c'). This is consistent with previous findings in the synthesis of TS-1 and other titanium-substituted molecular sieves in which the highest titanium incorporation in the 4-fold-coordinated silica framework is limited to a Si/Ti ratio of about 10.²¹

ZrMCM-41-(20) gives also a well-resolved XRD pattern typical of siliceous MCM-41 materials^{24,27} (not shown). As reported previously^{26b} for AIMCM-41-(30), the resolution of the XRD pattern deteriorates with increasing aluminum incorporation. This is interpreted as due to smaller particle sizes rather than a more disordered MCM-41 framework structure.

Electron microprobe analysis of V/TiMCM-41 shows that both titanium and vanadium are rather homogeneously distributed over a V/TiMCM-41 solid particle, which excludes the formation of either pure phase TiO₂ or V₂O₅. The Si/Ti ratios (Table 1) of TiMCM-41 increase linearly with increasing titanium content in the synthesis gel and are relatively close to that in the gel mixtures even in a sample with a Si/Ti ratio of 10. In possible contrast, the Si/Al ratio in V/AIMCM-41 shows significant deviation from the gel composition which should be studied further.

ESR. It has been reported that 4-fold-coordinated Ti⁴⁺ ions in zeolites can be reduced to Ti³⁺ upon thermal or CO reduction and give an ESR signal different from that in a 6-fold-coordinated environment.²⁸ In TiMCM-41, no ESR signal is detected even under more severe reduction conditions with H₂ or by ⁶⁰Co γ -irradiation. This different behavior of TiMCM-41 from other titanium-containing materials may be due to the dense wall structure of MCM-41²⁶ in which Ti³⁺ ions are difficult to reduce and stabilize. After vanadium is loaded onto the wall surfaces of MCM-41, various ESR signals of VO²⁺ ions are detected depending on the framework metal ion, vanadium content, and oxidation–reduction conditions.

Framework Metal Ions. Figure 2 shows the effect of different framework metal ions on the room temperature ESR spectra of

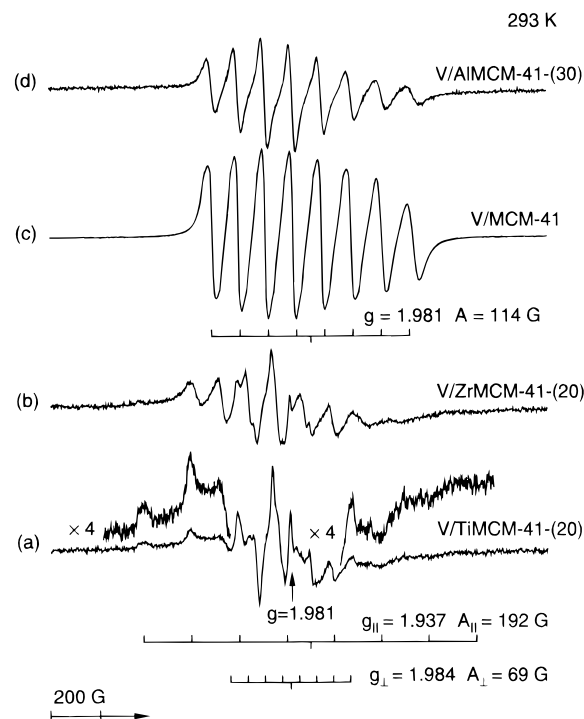


Figure 2. ESR spectra at 293 K of (a) V/TiMCM-41-(20), (b) V/ZrMCM-41-(20), (c) V/MCM-41 with a Si/V ratio of 60, and (d) V/AIMCM-41-(30) with a Si/V ratio 600.

VO²⁺ ions. ESR spectra of V/MCM-41 and V/AIMCM-41-(30) with either low (Figure 2d) or high vanadium loading (Figure 2c) consist of eight hyperfine lines originating from VO²⁺ species coupled to their own nuclear spin (⁵¹V, *I_n* = 7/2, natural abundance 99.8%) and can be described by the spin Hamiltonian parameter set *g* = 1.981 and *A* = 114 G, where *A* is the vanadium hyperfine coupling. This kind of ESR signal without anisotropy corresponds to free vanadyl (VO²⁺) ions,²⁹ which do not interact with the siliceous surface of MCM-41 or the aluminosilicate surface of AIMCM-41. This is further supported by the green color (Table 1).

In contrast, different spectroscopic features are observed in the ESR spectrum of V/TiMCM-41-(20) (Figure 2a), which shows strong anisotropy characterized by an axially symmetric set of eight lines described by the spin Hamiltonian parameters *g*_{||} = 1.937, *A*_{||} = 192 G and *g*_⊥ = 1.984, *A*_⊥ = 69 G. These *g* values and hyperfine coupling constants are typical of VO²⁺ complexes with square-pyramidal coordination,^{30,31} to which we assign this ESR signal. In addition, this ESR signal apparently overlaps a superimposed broad singlet with *g* = 1.981 assigned to a high local spin concentration of VO²⁺ ions. The anisotropic VO²⁺ complexes and VO²⁺ clusters occur only in TiMCM-41 and not in MCM-41 or AIMCM-41, so we suggest that these anisotropic VO²⁺ species are immobilized on titanium centers in TiMCM-41. Also, V/TiMCM-41-(20) changes its color from green of VO²⁺ to light yellow of V⁵⁺ immediately after vanadium loading in contrast to V/MCM-41 and V/AIMCM-41-(30) surfaces (Table 1), and the ESR signal intensity of VO²⁺ is weaker in V/TiMCM-41-(20) (Figure 2). Thus, an oxidation of VO²⁺ to V⁵⁺ catalyzed by titanium centers in V/TiMCM-41 is suggested, as further supported by UV–vis results below.

The same anisotropic ESR signal and color change are observed in V/ZrMCM-41-(20) (Figure 2b, Table 1), indicating that a surface interaction occurs also between vanadium and the zirconium centers of V/ZrMCM-41. But like in V/AIMCM-41 and V/MCM-41, some mobile isotropic VO²⁺ ions (*g* = 1.981 and *A* = 114 G) are also present in V/ZrMCM-41-(20).

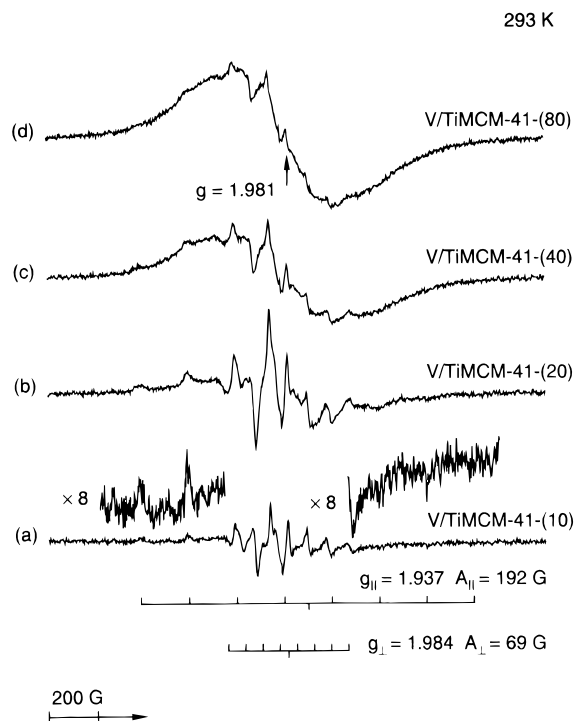


Figure 3. ESR spectra at 293 K (on the same scale) of V/TiMCM-41 with a Si/V ratio of 60: (a) V/TiMCM-41-(10), (b) V/TiMCM-41-(20), (c) V/TiMCM-41-(40), and (d) V/TiMCM-41-(80).

This indicates that the interaction between vanadium and surface centers in V/ZrMCM-41 is weaker than that in V/TiMCM-41.

Framework Si/Ti Ratio. Figure 3 shows room temperature ESR spectra of vanadium in V/TiMCM-41 with variable amounts of framework titanium. The vanadium loading on these samples is the same and equivalent to a Si/V ratio of 60. In V/TiMCM-41-(10) with a high framework titanium content, only isolated square-pyramidal VO^{2+} ions ($g_{||} = 1.937$, $A_{||} = 192$ G and $g_{\perp} = 1.984$, $A_{\perp} = 69$ G) are detected (Figure 3a), indicating monatomic dispersion of VO^{2+} ions at surface titanium centers. With decreasing framework titanium content some VO^{2+} clusters ($g = 1.981$) occur at the expense of isolated square-pyramidal VO^{2+} (Figure 3b,c) and become predominant in V/TiMCM-41-(80) (Figure 3d). This may suggest that each VO^{2+} species is immobilized at a surface titanium center at high titanium content and that more than two vanadium ions may interact at a single titanium center as the framework titanium content decreases.

A color change from green of VO^{2+} to light yellow of V^{5+} occurs immediately after vanadium is loaded onto V/TiMCM-41-(10), which has a high framework titanium content, but this is not so as the framework titanium content decreases (Table 1). This dependence of the color change upon framework titanium content supports the suggestion that titanium centers in V/TiMCM-41 serve as active sites for the oxidation of VO^{2+} to V^{5+} . More evidence will be provided by UV-vis (see below).

Vanadium Loading. Room temperature ESR spectra of V/TiMCM-41-(20) with variable vanadium loading are illustrated in Figure 4. At low vanadium loading equivalent to a Si/V ratio of 120, only monatomically dispersed VO^{2+} ions ($g_{||} = 1.937$, $A_{||} = 192$ G and $g_{\perp} = 1.984$, $A_{\perp} = 69$ G) are observed (Figure 4a), but with increasing vanadium loading a broad singlet ($g = 1.981$, $A = 114$ G) appears and becomes predominant (Figure 4b–e). Apparently, there exists a critical vanadium loading at which the largest monatomic surface

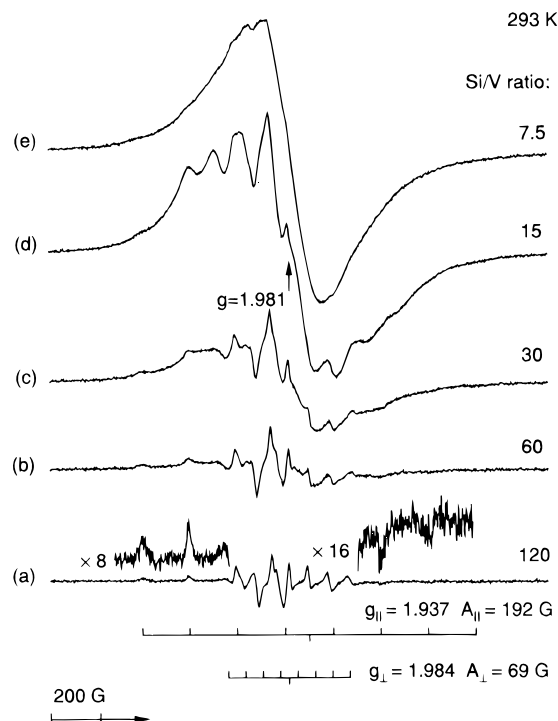


Figure 4. ESR spectra at 293 K (on the same scale) of V/TiMCM-41 with Si/V ratios of (a) 120, (b) 60, (c) 30, (d) 15, and (e) 7.5.

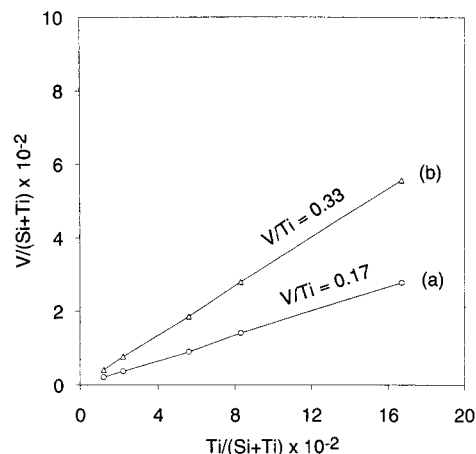


Figure 5. Dependence of the critical vanadium loading amount $V/(Si + Ti)$ on the framework titanium content $Ti/(Si + Ti)$ of V/TiMCM-41: (a) from ESR and (b) from diffuse reflectance UV-vis.

coverage of vanadium at titanium centers in TiMCM-41-(20) is achieved. For a series of TiMCM-41 samples such a value is determined from a plot of $V/(Si + Ti)$ versus $Ti/(Si + Ti)$ in Figure 5a. The critical vanadium loading $V/(Si + Ti)$ is apparently linearly proportional to the titanium content $Ti/(Si + Ti)$ with a critical V/Ti ratio of 0.17.

Redox Cycle of Monatomically Dispersed Vanadium Ions. As mentioned above, V/TiMCM-41-(20) with a Si/V ratio of 120 gives only an anisotropic ESR spectrum of vanadyl (Figure 6a). Upon calcination in static air at 550 °C this signal disappears completely (not shown) due to complete oxidation of VO^{2+} to tetrahedral V^{5+} , which corresponds to a color change from light green to white.

As this calcined sample is subjected to thermal reduction at 10^{-4} Torr at 200 °C, the corresponding ESR spectrum at room temperature (Figure 6b) shows reestablishment of the resolved hyperfine of isolated VO^{2+} ions, indicating reduction of V^{5+} to VO^{2+} species. These results suggest that the monatomically dispersed vanadium species shows a reversible redox cycle.

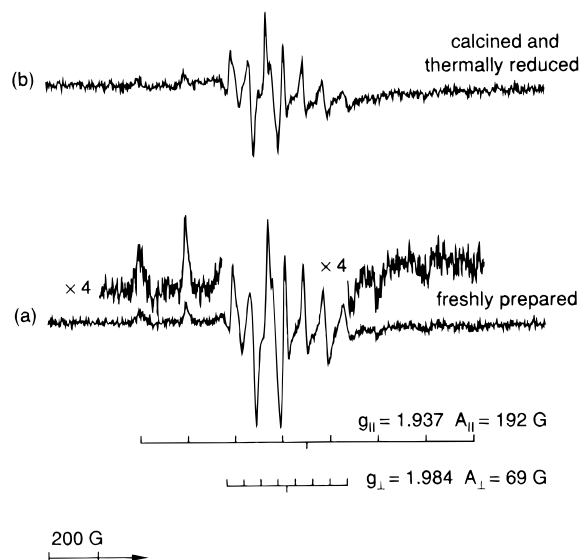


Figure 6. ESR spectra at 293 K (on the same scale) of V/TiMCM-41-(20) with a Si/V ratio of 60: (a) freshly prepared and (b) calcined and reduced forms.

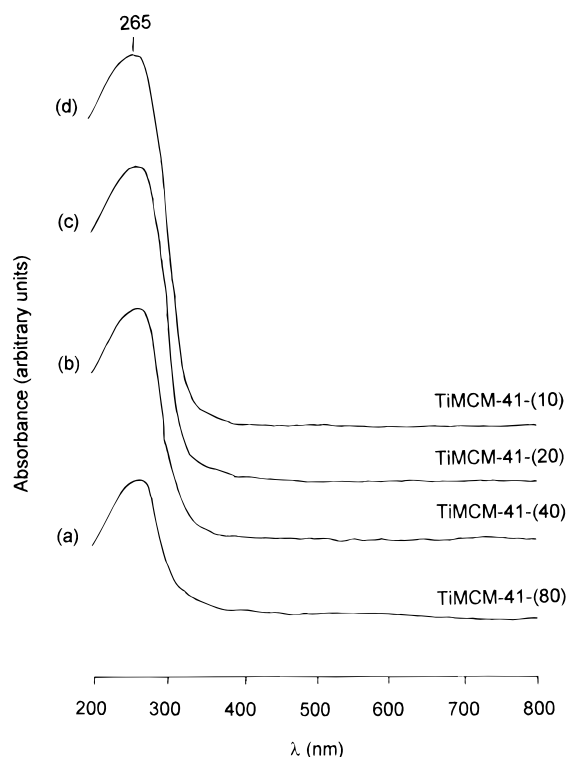


Figure 7. Diffuse reflectance UV-vis spectra of TiMCM-41 samples: (a) TiMCM-41-(80), (b) TiMCM-41-(40), (c) TiMCM-41-(20), and (d) TiMCM-41-(10).

UV-vis. TiMCM-41 Support. UV-vis spectroscopy has been extensively used to characterize the nature and coordination of Ti^{4+} ions in titanium-substituted molecular sieves.^{19–21,25} Figure 7 shows UV-vis spectra of TiMCM-41 with variable Si/Ti ratios. A broad band between 200 and 310 nm, centered at 265 nm, is observed in all samples, the intensity of which increases monotonically with increasing titanium content. Such a band can be assigned to a low-energy charge-transfer transition between tetrahedral oxygen ligands and central Ti^{4+} ions,²¹ indicating framework incorporation of titanium in MCM-41. A band between 300 and 350 nm is absent, indicating that an anatase-like phase is not formed in these samples during crystallization or upon calcination.²⁵ This result is consistent with previous characterization by XANES.²³

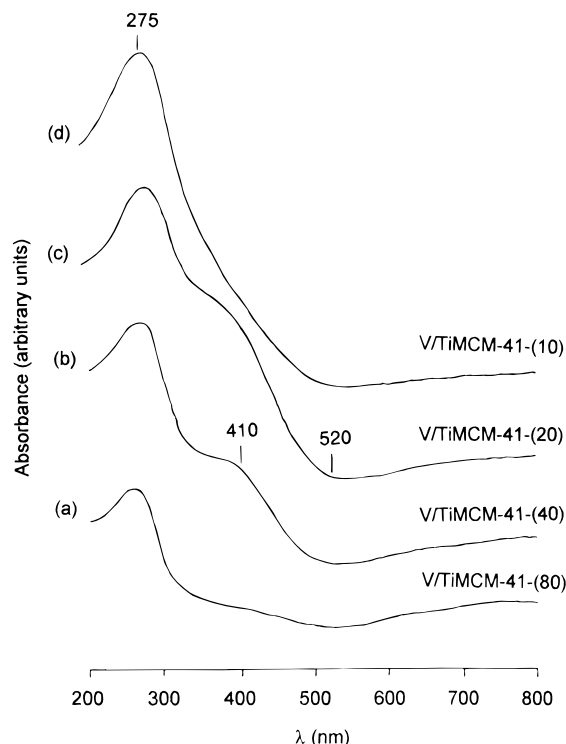


Figure 8. Diffuse reflectance UV-vis spectra of freshly prepared V/TiMCM-41 samples with a Si/V ratio of 60: (a) V/TiMCM-41-(80), (b) V/TiMCM-41-(40), (c) V/TiMCM-41-(20), and (d) V/TiMCM-41-(10).

Upon loading vanadium onto the walls of TiMCM-41 as well as onto other MCM-41 materials containing framework zirconium, aluminum, or silicon, quite different UV-vis spectroscopic features are observed depending on the framework metal ions, framework Si/Ti ratios, vanadium loading, and thermal treatments.

Framework Metal Ions. Without 4-fold-coordinated titanium or zirconium, both freshly prepared V/MCM-41 and V/AlMCM-41 are UV-vis silent, which along with the green color of VO^{2+} ions suggests that vanadium exists as in vanadyl sulfate solution and that the interaction of these VO^{2+} ions with the wall surfaces of MCM-41 or AlMCM-41 is weak. This is consistent with the ESR results. In the visible region no additional absorption bands, especially near 600 nm corresponding to the d-d transitions of vanadyl VO^{2+} ions,^{16,32} are detected. This is because the d-d transitions of vanadyl VO^{2+} ions are generally 10–30 times weaker than charge-transfer transitions³² and so are undetected in diffuse reflectance UV-vis.

However, with framework titanium a strong interaction between vanadium species and 4-fold-coordinated titanium is revealed by UV-vis as shown below. A similar interaction between vanadium species and surface zirconium centers is found in V/ZrMCM-41.

Framework Si/Ti Ratio. Freshly prepared V/TiMCM-41 in which the vanadium loading is the same and equivalent to a Si/V ratio of 60 gives quite complex UV-vis spectra depending on the framework Si/Ti ratio, as shown in Figure 8. In all samples the maximum of the 265 nm band of TiMCM-41 (Figure 7) slightly shifts to 275 nm in V/TiMCM-41 (Figure 8) but does not show any change in intensity. Another broad band centered at 410 nm appears in V/TiMCM-41 with low framework titanium content (Figure 8a) and increases with increasing titanium content (Figure 8b,c). A charge-transfer transition near 410 nm can be assigned to a V^{5+} species with square-pyramidal coordination,^{33,34} indicating that some VO^{2+} ions have been

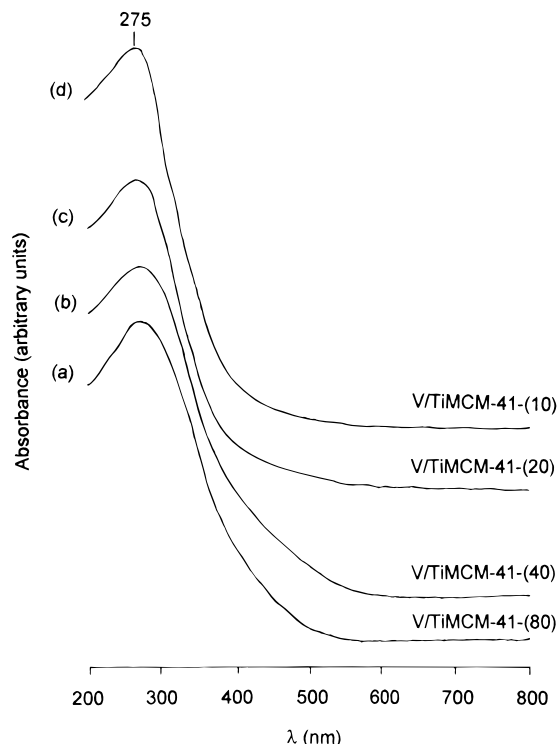


Figure 9. Diffuse reflectance UV-vis spectra of freshly calcined V/TiMCM-41 samples with a Si/V ratio of 60: (a) V/TiMCM-41-(80), (b) V/TiMCM-41-(40), (c) V/TiMCM-41-(20), and (d) V/TiMCM-41-(10).

oxidized to V^{5+} and have become 5- and/or 6-coordinated by additional coordination with water molecules. This is consistent with the color change of these samples from green to yellow with increasing framework titanium content (Table 1). Since such an oxidation of VO^{2+} to V^{5+} occurs only after siliceous MCM-41 has titanium incorporated and is enhanced by increasing the framework titanium content, these vanadium species apparently interact with titanium centers in V/TiMCM-41. The addition of water molecules into the coordination sphere of V^{5+} ions indicates a relatively weak bonding between the vanadium species and the titanium centers of TiMCM-41. Further increase of titanium content as the Si/Ti ratio approaches 10 causes the 410 nm band to decrease, and the sample shows a UV-vis spectrum similar to TiMCM-41-(10) (Figure 8d). However, the color change of V/TiMCM-41-(10) from green of VO^{2+} ions to white of tetrahedral V^{5+} ions indicates that oxidation of VO^{2+} to V^{5+} also occurs and that these V^{5+} ions are strongly bonded to the titanium centers of TiMCM-41.^{30–34} These results suggest that at low titanium content V^{5+} ions may accumulate at titanium centers of TiMCM-41 as clusters and become monatomically dispersed as surface titanium centers increase to match the number of vanadium ions.

Upon calcination in static air all V/TiMCM-41 samples are white due to complete oxidation of the vanadium species to V^{5+} ions and give the same shape UV-vis spectra (Figure 9) in which only the 275 nm band is resolvable. Upon exposure to moist air (67% relative humidity at about 23 °C), samples with low framework titanium content are orange and become yellow or light yellow with increasing framework titanium content (Table 1) as reflected by the broadening of the UV-vis spectrum toward lower energy (Figure 10a–c). Repeated calcination and exposure to moist air show that both the color and UV-vis spectral changes of these V/TiMCM-41 samples are reversible. As the framework titanium content increases to a Si/Ti ratio of 10, no apparent change either in color or UV-vis spectra is observed during this calcination-rehydration

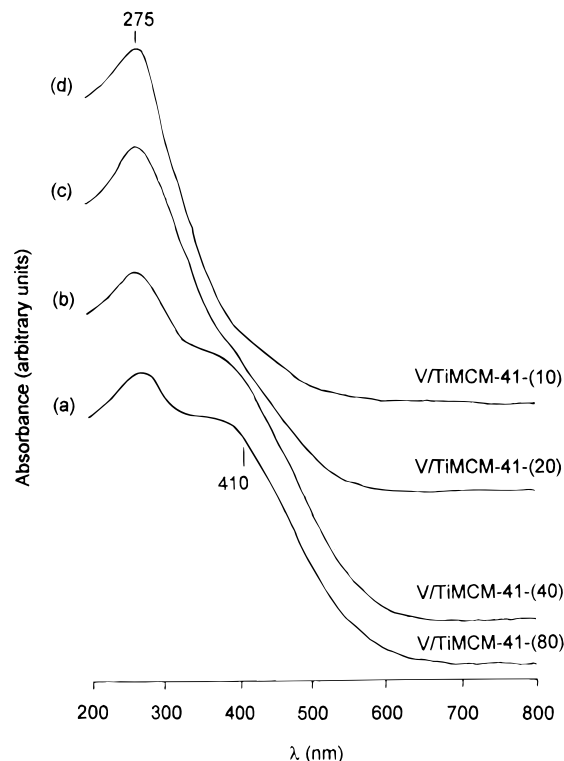


Figure 10. Diffuse reflectance UV-vis spectra of calcined-rehydrated V/TiMCM-41 samples with a Si/V ratio of 60: (a) V/TiMCM-41-(80), (b) V/TiMCM-41-(40), (c) V/TiMCM-41-(20), and (d) V/TiMCM-41-(10).

procedure (Figures 9d and 10d, Table 1). This indicates that the monatomically dispersed vanadium species at titanium centers are stable.

The shape of the UV-vis absorption in the range 200–400 nm (Figures 8–10) deserves further comment. The 4-fold-coordinated V^{5+} ions give intense absorption in this range due to charge-transfer transitions between tetrahedral oxygen ligands and central V^{5+} ions.^{30–35} A 290 nm band occurs when the V^{5+} ions are located in a relatively symmetric environment of four nearly equivalent oxygen ligands and is typical for framework V^{5+} ions in zeolites.³⁵ Another band at 340 nm also due to 4-fold-coordinated V^{5+} has been observed in supported V_2O_5 catalysts.³⁶ A recent study showed that cubic silica MCM-48 material with surface grafted vanadium centers gives a 340 nm band.³⁷ In V/TiMCM-41 samples no contribution from either of these two bands is observed in freshly prepared samples, but after calcination V^{5+} ions seem to give additional absorption at 275 nm when the framework titanium content is low and vanadium clusters may exist (Figure 9). This contribution decreases and becomes unobservable with increasing framework titanium content. (See Figure 7 and note the increasing absorption from Ti^{4+} .) This may suggest that there exists specific interaction between surface titanium centers and immobilized vanadium species. Additional comment may also be made about the 520 nm band in Figure 8. It appears in freshly prepared V/TiMCM-41 with low titanium content where VO^{2+} clusters occur as shown by ESR (Figure 3) and disappears after calcination. It seems to originate from an interaction between the VO^{2+} clusters and the titanium centers.

Vanadium Loading. Figure 11 shows UV-vis spectra for V/TiMCM-41-(20) with variable vanadium loading. At a low vanadium loading with Si/V equal 120, only a 275 nm band is observed (Figure 11a), the intensity of which is equivalent to that of TiMCM-41-(20) (Figure 7c). No other UV-vis absorption, especially at 410 nm for square-pyramidal V^{5+} ions, is

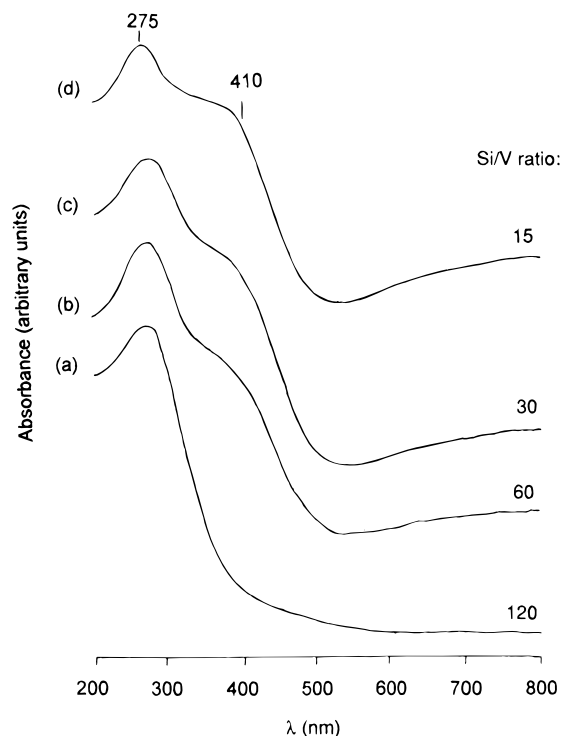


Figure 11. Diffuse reflectance UV-vis spectra of freshly prepared V/TiMCM-41(20) with Si/V ratios of (a) 120, (b) 60, (c) 30, and (d) 15.

resolvable, indicating an monatomic dispersion of vanadium on the titanium centers. With increasing vanadium loading to a Si/V ratio lower than 60, the 410 nm band becomes resolvable in addition to the 275 nm band, and its intensity increases (Figure 11b–d), indicating that V^{5+} clusters are formed at high vanadium loading.

After calcination and rehydration, the 410 nm band becomes predominant in the UV-vis spectra of samples with high vanadium loading due to the oxidation of VO^{2+} to V^{5+} (Figure 12c,d), while this band is not resolvable for low vanadium loading (Figure 12a). A sample with Si/V equal 60 gives a less intense 410 nm band in its calcined form than in its as-synthesized form. It seems that calcination promotes a higher dispersion of vanadium on the wall surfaces of TiMCM-41. A critical Si/V ratio at which the highest vanadium loading is achieved without resolving a 410 nm band in the UV-vis spectrum has been determined from calcined-rehydrated V/TiMCM-41 samples and is depicted as a plot of $V/(Si + Ti)$ against $Ti/(Si + Ti)$ in Figure 5b. Compared to a critical V/Ti ratio of 0.17 from ESR data for as-synthesized samples, the value increases to approximately 0.33 from UV-vis data for calcined samples. This is interpreted as meaning that a greater dispersion of vanadium occurs on calcination.

Discussion

For a series of V/TiMCM-41 samples with variable Si/Ti ratios, ESR and UV-vis spectroscopies indicate a critical vanadium loading corresponding to a V/Ti ratio of about 0.17 for freshly prepared samples and about 0.33 for calcined and rehydrated samples at which monatomic coverage of surface titanium centers by vanadium is achieved. Overloading vanadium above these values results in more than two vanadium ions at a single titanium center of TiMCM-41 and the occurrence of VO^{2+} and V^{5+} clusters. Assuming uniform dispersion of 4-fold-coordinated titanium in the hexagonal walls of TiMCM-41 and about 2.5 Å between two T atoms,³⁸ where T represents

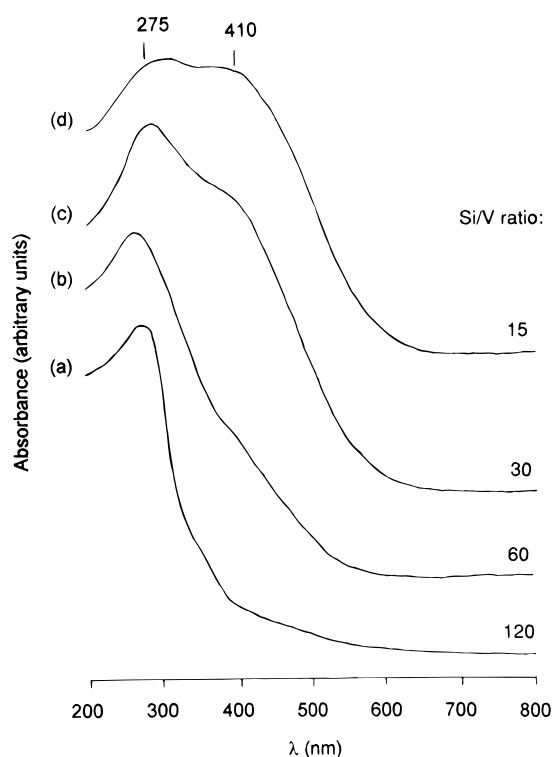


Figure 12. Diffuse reflectance UV-vis spectra of calcined-rehydrated V/TiMCM-41(20) with Si/V ratios of (a) 120, (b) 60, (c) 30, and (d) 15.

Si^{4+} or Ti^{4+} , about 20% of the titanium atoms are on the wall surfaces of TiMCM-41, assuming 10 Å thick walls. This is compatible with the critical V/Ti ratio. A recent study on AlMCM-41 with the same structural dimensions showed that about 44% of the aluminum sites are exchangeable for Cu(II) ions, indicating a higher fraction of metal ion rather than silicons on the wall surfaces.³⁹

Some aspects of the structure of the vanadium species in V/TiMCM-41 can be suggested from previous studies of supported vanadium oxide catalysts involving ^{51}V NMR and Raman spectroscopy. We do not have solid state NMR facilities, but we have run a few samples elsewhere. Unfortunately, the ^{51}V NMR spectra are very poorly resolved due to the low V^{5+} concentration.

Structure of Surface Vanadium Species in V/TiMCM-41.

^{51}V NMR and Raman spectroscopies of V_2O_5/TiO_2 show that at low surface coverage the vanadium species is apparently 4-fold-coordinated with one terminal $V=O$ bond and three $V-O$ bonds to the support.^{12,14} The bridging oxygens to the support may be 3-coordinated and present as $V-O(-Ti)_2$ which is different from the 2-coordinated $V-O-Si$ bridging oxygen in V_2O_5/SiO_2 . For V/TiMCM-41 with low vanadium loading, a 3-coordinated bridging oxygen structure $V-O(-Ti)_2$ seems improbable since the titanium is also monatomically dispersed, and the wall surface is dominated by silicon. Thus, a different vanadium structure consisting of one terminal $V=O$ bond, one $V-O$ -titanium bond, and two $V-O$ -silicon bonds or $(Si-O)_2V=O(-O-Ti)$ is suggested. Titanium in V/TiMCM-41 is 4-fold-coordinated, which may cause modification of the $V-O$ bond to the support.

For increasing surface vanadium oxide coverage ^{51}V NMR and Raman spectroscopies of V_2O_5/TiO_2 suggest a transformation from monomeric vanadium species to polymeric surface vanadium oxide species.¹⁷ Similar vanadium structures may also be present in V/TiMCM-41 at higher vanadium loading. However, these vanadium clusters are still isolated and relatively

weakly bonded to the titanium centers of TiMCM-41 as shown by ESR and UV-vis spectroscopies.

Dependence of Surface Vanadium Species on Framework Metal Ions. Since our results reveal that the vanadium is also immobilized at zirconium centers in V/ZrMCM-41, a similar vanadium species can be suggested for V/ZrMCM-41. However, the bonding between vanadium and the surface zirconium centers seems weaker than that between vanadium and surface titanium centers in V/TiMCM-41. In V/MCM-41 and V/AlMCM-41 without 4-fold-coordinated titanium or zirconium, vanadium exists as free vanadyl ions in freshly prepared samples and mainly as 5- and/or 6-coordinated species in calcined and rehydrated samples, indicating that vanadium does not strongly interact with the siliceous surface of MCM-41 or aluminosilicate surface of AlMCM-41.

The physical characteristics of the surface vanadium oxide species are clearly influenced by the surface reducibility of metal-substituted MCM-41 materials which follows the reducibility of the pure metal oxide.¹⁴ For example, titanium in TiO₂ is readily reduced at both bulk and surface sites, and zirconium in ZrO₂ is readily reduced only at its surface sites. For both Al₂O₃ and SiO₂ such a reduction does not occur.

Suitability for Selective Catalytic Reduction. Previous selective catalytic reduction reactivity studies of supported vanadium catalysts demonstrated that dispersed surface vanadium species undergo a partial reduction from V⁵⁺ to VO²⁺ in the reaction stream, and the intrinsic reaction activation energy and turnover frequency coincide with the vanadium reoxidation activation energy. Thus, the reoxidation of the reduced vanadium species by lattice oxygen from underlying layers is suggested to be the rate-limiting step for selective catalytic reduction.^{6,8} This is supported by the fact that the highest activity is obtained from V₂O₅/TiO₂ in a series of supported vanadium catalysts, in which the TiO₂ support has the highest reducibility. The titanium may play an important role in electron-transfer process between surface vanadium species to the TiO₂ support.

In V/TiMCM-41 monatomically dispersed vanadium shows strong catalytic promotion by Ti for the oxidation of VO²⁺ to V⁵⁺, and this oxidation-reduction cycle is reversible. Thus, V/TiMCM-41 may be useful as an effective catalyst for selective catalytic reduction reactions. The large wall surface of TiMCM-41 and the activated vanadium species structure suggest that V/TiMCM-41 may have advantages over other supported vanadium oxide catalysts.

Conclusions

A combination of ESR and UV-vis spectroscopies has been used successfully to characterize the chemical environment of vanadium in V/TiMCM-41. The results reveal a strong interaction between vanadium and surface titanium centers which immobilizes the vanadium species and promotes the oxidation of VO²⁺ to V⁵⁺. At lower vanadium loading than a critical V/Ti ratio of 0.17 vanadium is monatomically dispersed at surface titanium centers, whereas at higher vanadium loading two vanadium species coordinate to a single titanium center, resulting in the formation of some vanadium clusters. Calcination causes the critical V/Ti ratio to increase to 0.33, indicating that calcination enhances dispersion of vanadium at surface titanium centers of TiMCM-41. Thermal reduction demonstrates that monatomically dispersed vanadium species can engage in reversible redox cycles. A similar surface interaction is found between vanadium and surface zirconium centers in V/ZrMCM-41, but not with silicon or aluminum in V/MCM-41 or V/AlMCM-41. This is interpreted as due to the different reducibilities of these framework metal ions.

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