

Photoluminescence Study of the Introduction of V in Si-MCM-41: Role of Surface Defects and Their Associated SiO[−] and SiOH Groups

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The photoluminescent properties of highly ordered siliceous and vanadium-substituted mesoporous molecular sieves (MCM-41) are examined. Both Si-MCM-41 and V-loaded MCM-41 show green/blue/violet photoluminescence at 490–400 nm, likely due to surface defects associated with SiO[−] and/or SiOH groups. The intensity of the green/blue/violet emission strongly decreases when MCM-41 materials contain well-dispersed tetrahedral V^V species. This intensity decrease is related to the consumption of surface defects and their associated SiO[−] and/or SiOH groups. Photoluminescence spectroscopy distinguishes only one kind of tetrahedral V^V species, characterized by a vibrational fine structure and energy corresponding to a short V=O bond. The intensity of photoluminescence from vanadyl groups in V-loaded MCM-41 increases as a function of V content. The addition of an anti-foaming agent into the synthesis solution enhances reproducibility of V-MCM-41 materials and causes a highly ordered hexagonal MCM-41 structure. The local symmetry of vanadium ions dispersed in highly ordered MCM-41 structure is closely related to the pore size of the mesoporous matrix.

Introduction

It is well-known¹ that the catalytic and physicochemical properties of microporous materials, such as zeolites, can be affected by the presence of framework defects. Recently, much research has been focused on the investigation of structural defects in mesoporous molecular sieves, in particular MCM-41.^{2–5} Luan et al.³ have reported that ²⁹Si MAS NMR spectra of siliceous hexagonal structured MCM-41 materials are identical to those of amorphous silica, indicating an irregular arrangement of Si–O–Si bonds and a wide range of bond angles in the pore walls. Beck et al.⁶ have reported that about 14% of silicon atoms in MCM-41 are in the form of siloxy groups (SiO[−]), which play a charge balancing role for the cetyltrimethylammonium (CTMA) template agent used in the synthesis. These siloxy groups can be protonated during calcination of MCM-41 with formation of silanol groups. Feuston and Higgins⁷ have reported that the silanol content in siliceous MCM-41 is in the range 17–28%. Species such as SiO[−] and/or SiOH groups may play an important role in the incorporation of transition metals in the mesoporous structure of MCM-41 materials, as has been previously reported for zeolites.^{8–13}

In recent years, increasing attention has been focused on the introduction of transition metals into MCM-41^{6,14–18} and on the use of the resulting materials as catalysts in various types of reactions.^{19–22} The incorporation of metals into MCM-41 leads to a decrease of the pore size and a broadening of the pore size distribution in comparison with those of the parent MCM-41.^{23a} The perturbation of pore size is hypothesized to be dependent

on the coordination of metal with OH groups.^{23b} Recently,^{23c} a highly ordered V-substituted MCM-41 has been prepared and characterized by ⁵¹V NMR, FTIR, XRD, N₂ physisorption, and TPD. The amount of V incorporated increased with the chain length of the surfactant used as templating agent. It was also suggested that this phenomenon is related to the V–O–Si bond angle. If the chain length of surfactant is long enough, it can lead to a large pore channel, and incorporated V may be arranged along the pore channel more easily than in the small pore channel templated by a short chain length surfactant.^{23b} Determination of the exact nature of the V species in V-loaded MCM-41 materials requires further spectroscopic studies.

In this paper, we report photoluminescence measurements on siliceous and vanadium-loaded MCM-41 in order to obtain more information about the properties of defects associated with silanol groups present in such materials, and to better understand the vanadium environment in a series of highly ordered V-MCM-41 materials. Moreover, analysis of the green/blue/violet photoluminescence at 490–400 nm in Si-MCM-41²⁴ and V-MCM-41 materials suggests that incorporation of V in the MCM-41 structure involves the surface defects and their associated SiO[−] and/or SiOH groups.

Experimental Section

Materials. A typical preparation for the vanadium-MCM-41 synthesis gel involved mixing reagents in the following molar ratios, SiO₂/surfactant/V/H₂O = 1:0.27:0.017:55.7. The silica sources were Hisil-233 (or Hisil-915) from Pittsburgh Plate Glass (PPG) and tetramethylammonium silicate (10 wt % silica, SACHEM Inc.). Vanadyl sulfate hydrate (99.99+ % VOSO₄ × 3H₂O) from Aldrich Chemical Co. was the V precursor. Quaternary ammonium surfactants C_nH_{2n+1}(CH₃)₃NBr were purchased from Sigma Co. with *n* = 12 and 14 and from American Tokyo Kasei with *n* = 10. The C_nH_{2n+1}(CH₃)₃NOH (*n* = 10, 12, 14) solutions were prepared by ion exchanging a

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TABLE 1: V Content in V-MCM-41 Samples (data from ref 23c)

samples	analysis	V wt %
C10 V-MCM-41 (H ₂ O/Si mole ratio = 55.7)	vanadium	0.41
C12 V-MCM-41 (H ₂ O/Si mole ratio = 55.7)	vanadium	0.92
C14 V-MCM-41 (H ₂ O/Si mole ratio = 55.7)	vanadium	1.10

29 wt % C_nH_{2n+1}(CH₃)₃NBr aqueous solution with equal molar exchange capacity of Amberjet-400 (OH) ion-exchange resin (Sigma Co.) via overnight batch mixing. The anti-foaming agent was Antifoam A from Sigma Co., a silane polymer alkyl-terminated by methoxy groups. Acetic acid (Fisher Scientific) was used for pH adjustment of synthesis solutions.

Synthesis. Siliceous and vanadium-substituted MCM-41 materials were synthesized as described earlier.^{23c} Hisil-233, tetramethylammonium silicate, and the vanadium aqueous solution were mixed for 30 min. The surfactant C_nH_{2n+1}(CH₃)₃-NOH (*n* = 10, 12, 14) solutions were added and a small amount of anti-foaming agent (two drops with spatula) was introduced to remove excess foam produced by the surfactant and to improve of reproducibility of V-MCM-41 materials.^{23c} To investigate the effect of pH adjustment, acetic acid was added until pH = 11. After additional mixing for 10 min, this synthesis solution was poured into a polypropylene bottle and placed in an autoclave at 100 °C for 6 days. After cooling to room temperature, the resulting solid was recovered by filtration, washed with deionized water, and dried under ambient conditions. The solid was then heat-treated from room temperature to 540 °C over 20 h in flowing He, then for 1 h at 540 °C in flowing He, and finally for 5 h at 540 °C in flowing air to remove the residual surfactant. The samples are labeled C10 V-MCM-41, C12 V-MCM-41, and C14 V-MCM-41.

A V-free siliceous MCM-41 material was prepared using the same procedure without addition of VOSO₄·3H₂O into the synthesis solution. Chemical analysis of V-MCM-41 samples was performed by inductively coupled plasma spectrometry (ICP) (Galbraith Laboratories, Inc.) and the results are reported in Table 1.

Methods. Photoluminescence measurements were performed at 77 K with a Spex Fluorolog II spectrofluorimeter. Prior to photoluminescence measurements, powdered Si-MCM-41 and V-loaded MCM-41 samples (C10, C12, and C14 V-MCM-41) were placed in a quartz cell with window and furnace sections that were connected to a vacuum line and outgassed at 473 K for 2 h at pressure of 10⁻³ Pa. Photoluminescent properties of calcined (template-free) Si-MCM-41 and V-MCM-41 were examined using ultraviolet photons with energies higher than 3.5 eV. Emission spectra were recorded using 250, 257, or 305 nm excitation light and emission band-pass of 0.5 nm, to better distinguish the vibrational fine structures. Excitation spectra were recorded by monitoring the 520 nm emission light.

Results

As shown by XRD and nitrogen physisorption data,^{23c} all samples used in this study have a highly ordered hexagonal structure. The pore sizes of samples prepared with different surfactants were found to increase with the surfactant chain length from 18.2 to 25.9 Å.^{23c} In addition, the amount of vanadium introduced in the mesoporous material upon synthesis increases with surfactant chain length (Table 1) (data from ref 23c).

The samples showed similar ⁵¹V NMR patterns and the main signals at about -520 ppm were assigned to tetrahedral vanadium. Octahedral vanadium ions were not detected (absence

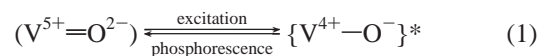
of signals around -300 ppm). Lim and Haller^{23c} have suggested that most of the vanadium ions are substituted into the mesoporous framework in tetrahedral coordination with surrounding oxygen anions.

Because of the high sensitivity of luminescent sites to their local environment,^{12,25,26} photoluminescence spectroscopy was used to obtain precise information about the properties of surface defect sites in Si-MCM-41 and the symmetry of the tetrahedral V species in V-MCM-41 materials.

Photoluminescence of Siliceous MCM-41. Figure 1 shows both the excitation and photoluminescence spectra of Si-MCM-41. The excitation spectrum exhibits two broad bands at around 235 and 285 nm (Figure 1A). These absorption bands correspond to emission bands at about 425 and 470 nm (Figure 1B). The spectral distribution of the Si-MCM-41 photoluminescence, obtained at 250 nm excitation light, is shown in Figure 1B. Three very broad emission bands appear with maxima near 425, 470, and 620 nm. Similar emission bands at 420 nm, 470 nm, and 600–640 nm were recently reported for siliceous MCM-41 and amorphous silica.²⁴ These emission bands are likely due to surface defects associated with SiO⁻ and/or SiOH groups, in agreement with recently published data.^{27–29} Oxides such as alumina, MgO, and zeolites, with high amounts of surface OH groups, show the same or very similar photoluminescence spectra.^{12,29,30}

Photoluminescence of V-MCM-41. Figure 2 shows both the excitation and photoluminescence spectra of V-MCM-41 materials. The excitation spectra of all V-MCM-41 powders (C10, C12, and C14 V-MCM-41 samples) exhibit two broad bands at around 250 and 300 nm (Figure 2A), whose shapes and positions as well as relative intensities strongly depend on the surfactant chain length and/or V content. The intensities of these bands increase in the series C10, C12, and C14 V-MCM-41.

Figure 2B shows the phosphorescence spectra of all V-MCM-41 samples. The photoluminescent properties of V-MCM-41 samples change with V content and strongly depend on the surfactant chain length used for their preparation. The C10, C12, and C14 V-MCM-41 exhibit characteristic photoluminescence spectra with maxima at around 450–550 nm together with a vibrational fine structure due to the V=O bond. These excitation and phosphorescence spectra, which are in good agreement with those obtained with well-dispersed V species on silica and zeolite materials,^{12,31–38} can be attributed to charge-transfer processes (eq 1) related to surface vanadyl groups of tetrahedral V. These processes involve an electron transfer from O²⁻ (ligand) to V⁵⁺ (metal) and a reverse radiative decay from the charge-transfer excited triplet state.²⁵



The vibrational fine structure of the phosphorescence spectrum corresponds to a transition from the lowest vibrational level of the excited triplet state T₁{V⁴⁺-O⁻}* to the various vibrational levels of the ground singlet state S₀(V⁵⁺=O²⁻).²⁵ The positions of the components of the fine structure for C10 and C12 V-MCM-41 are very close to those observed for amorphous V/SiO₂.³⁸ For C14 V-MCM-41, the components of the vibrational fine structure are observed at higher wavelengths. The intensity of the components increases with V content in the series C10, C12, and C14 V-MCM-41. For C10 V-MCM-41, the vibrational fine structure is not very well-resolved. A broad band at around 390–430 nm suggests the presence of a relatively important amount of surface defects associated with SiO⁻ and/or SiOH groups. In contrast, for C12 and C14 V-MCM-41 the bands are more intense and better resolved.

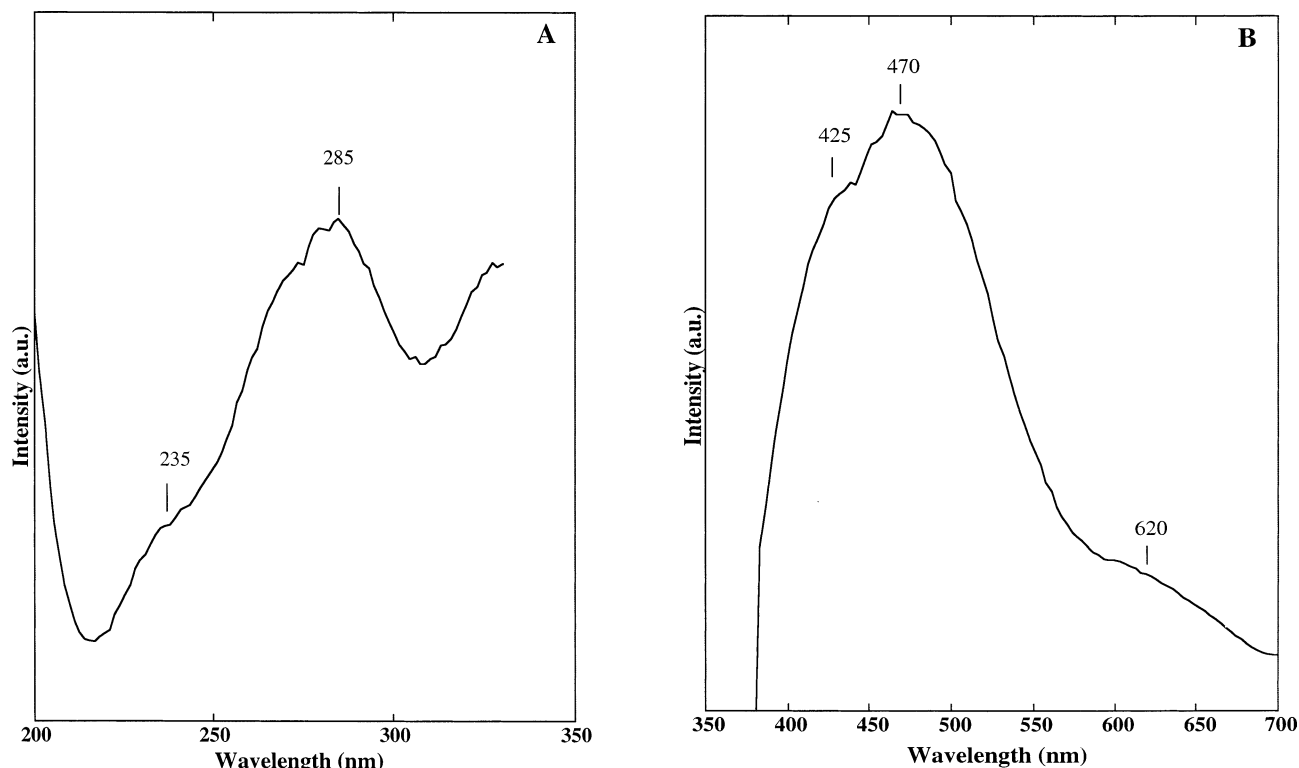


Figure 1. Excitation (A) and photoluminescence (B) spectra at 77 K of Si-MCM-41 outgassed at 473 K for 2 h (10^{-3} Pa). The excitation spectrum was recorded by monitoring the 520 nm emission band. The photoluminescence spectrum was obtained using irradiation of 250 nm light.

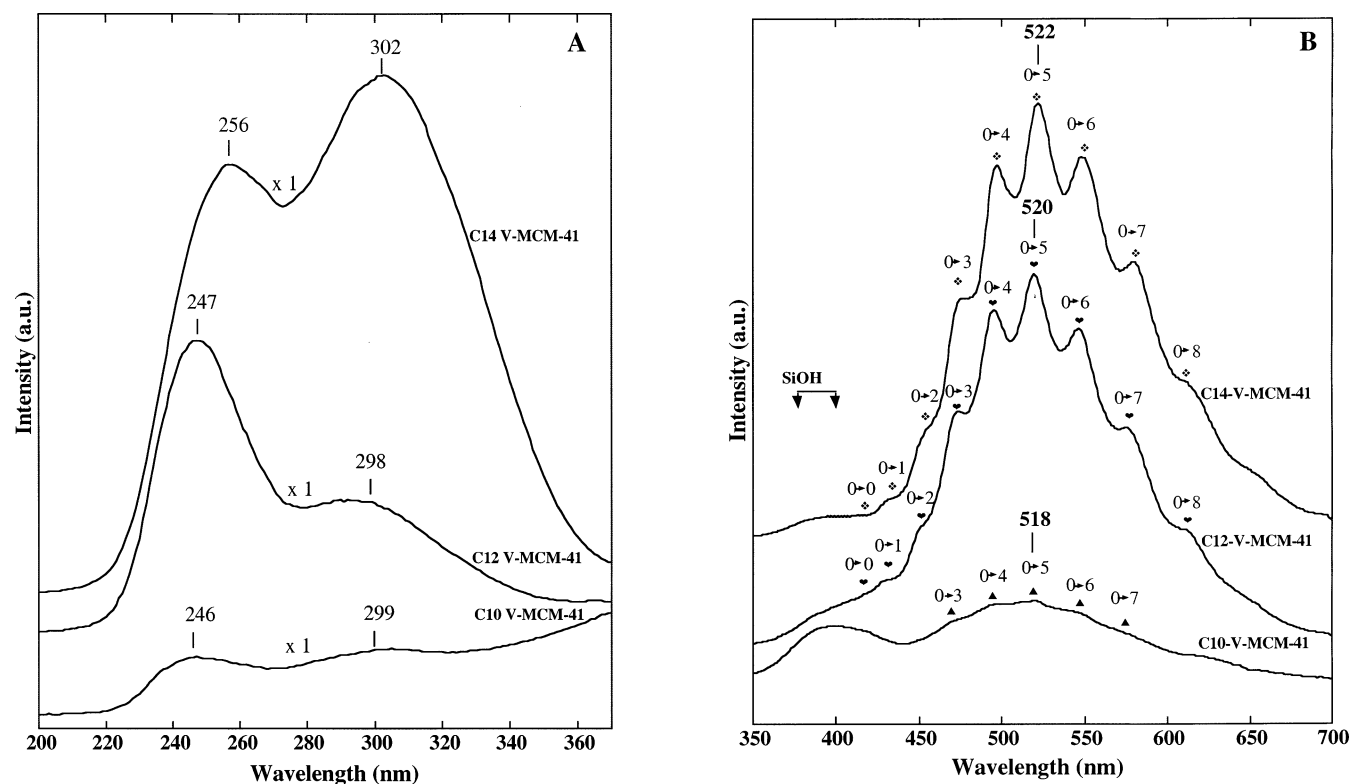


Figure 2. Excitation (A) and photoluminescence (B) spectra at 77 K of V-MCM-41 outgassed at 473 K for 2 h (10^{-3} Pa). The excitation spectra were recorded by monitoring the 520 nm emission band. The photoluminescence spectra were obtained using irradiation of 250 nm light.

For all V-MCM-41 materials, the intensity of the photoluminescence spectra increases as the excitation is changed from 250 to 305 nm. This is in agreement with earlier data obtained for siliceous MCM-41.²⁴ Figures 3 and 4 show this increase as a function of the excitation wavelength for C10 V-MCM-41

and C14 V-MCM-41, respectively. For C10 V-MCM-41, the vibrational fine structure is not well-resolved when using either 250 and 305 nm excitation light. In contrast, for C14 V-MCM-41, the photoluminescence spectra show very well-resolved vibrational fine structure. The bands are most intense after

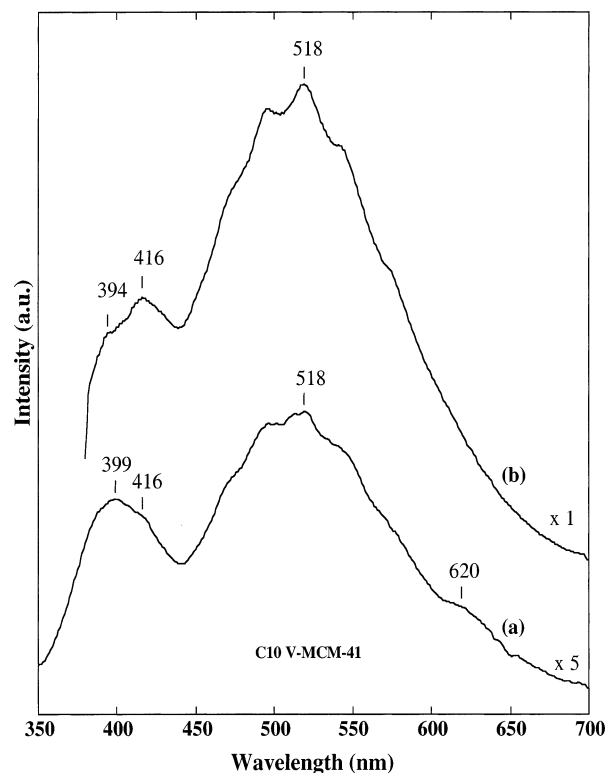


Figure 3. Photoluminescence spectra at 77 K of C10 V-MCM-41 outgassed at 473 K for 2 h (10^{-3} Pa). Emission spectra recorded using excitation light at 250 (a) and 305 (b) nm.

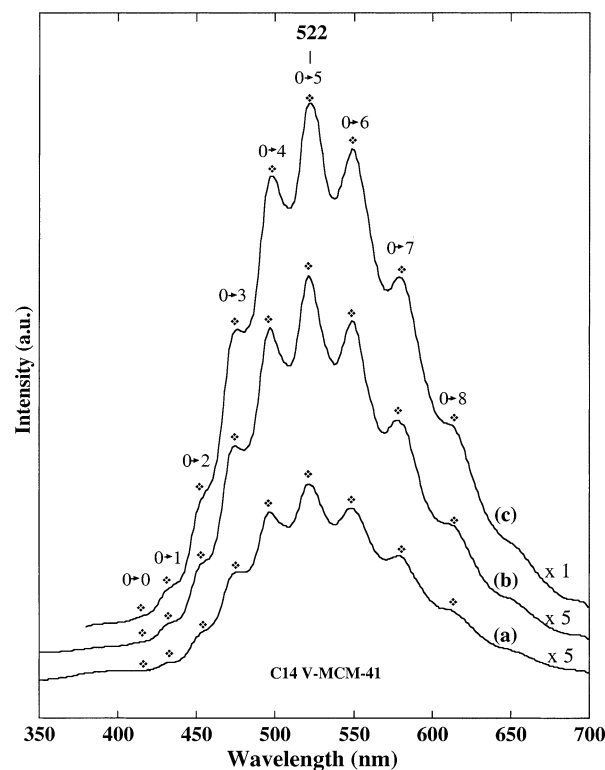


Figure 4. Photoluminescence spectra at 77 K of C14 V-MCM-41 outgassed at 473 K for 2 h (10^{-3} Pa). Emission spectra recorded using excitation light at 250 (a), 257 (b) and 305 (c) nm.

excitation at 305 nm. They are not affected by photoluminescence due to surface defects, and the energy separation between the different vibrational transitions can thus be determined for tetrahedral V species.

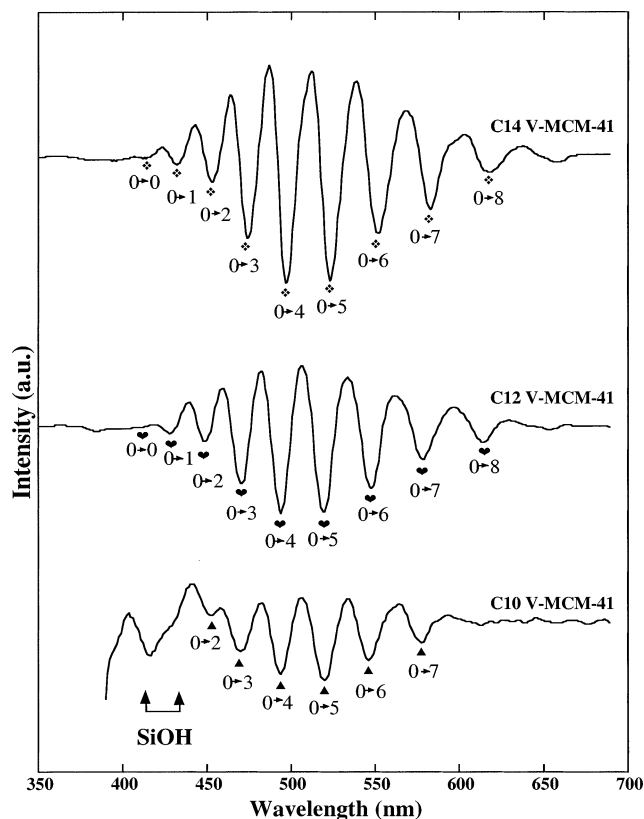


Figure 5. Second derivative of the photoluminescence spectra at 77 K of C10, C12, and C14 V-MCM-41 outgassed at 473 K for 2 h (10^{-3} Pa). Emission spectra recorded using excitation light at 250 (for C12 and C14 V-MCM-41 samples) and 305 (for C10 V-MCM-41 sample) nm.

To better analyze photoluminescence spectra, in particular that of C10 V-MCM-41 which is not well-resolved, the second derivative is used. For C10 V-MCM-41, only one well-resolved vibrational fine structure is observed after excitation at 250 nm (Figure 5.). Similar emission spectra of the surface vanadyl groups have been previously reported for V_2O_5 supported on SiO_2 , MgO , γ - and α - Al_2O_3 ,³³ and on porous Vycor glass.^{31,32} A very good separation of the maxima in the second derivative photoluminescence spectrum allows one to determine the different transitions. The use of second derivative spectra to ease the analysis of luminescence data has been previously reported for V/SiO_2 ,^{25,26,38} and $VSi\beta$,^{12,36,37} $VS-2$,^{39,40} and $VZSM41$ zeolites. The intensity of the second derivative photoluminescence spectrum of C10 V-MCM-41 increases as the excitation is changed from 250 to 305 nm (spectrum not shown). Moreover, the positions of the peak maxima do not change upon varying the excitation UV wavelength. It suggests that two maxima observed in the excitation spectra near 250 and 300 nm (Figure 2) are likely to be due to the same kind of V species.

In contrast, second derivative photoluminescence spectra of C12 and C14 V-MCM-41 (Figure 5) are not affected by the photoluminescence of surface defects. The energy separation between $(0 \rightarrow 0)$ and $(0 \rightarrow 1)$ vibrational transitions can thus be determined for V species, in good agreement with the vibrational energy of the surface $V=O$ bond obtained by IR and Raman measurements for various oxide-supported vanadium catalysts: V_2O_5/SiO_2 ,^{25,33,38,42} V_2O_5/PVG ,^{25,31,32,43} V_2O_5/γ - Al_2O_3 ,³³ and $VSi\beta$ zeolite.^{12,36,37} The vibrational energy calculated from the second-derivative spectra of C12 V-MCM-41 corresponds to 1042 cm^{-1} , a value very close to that found earlier for V species (θ species) on V/SiO_2 .³⁸ On the basis of the linear correlation between the wavenumber of the $V=O$ bond

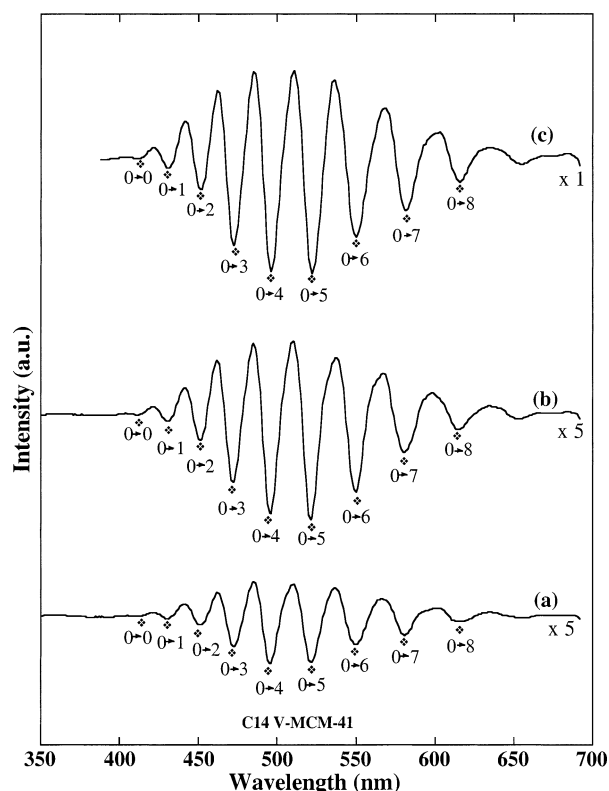


Figure 6. Second derivative of the photoluminescence spectra at 77 K of C14 V-MCM-41 outgassed at 473 K for 2 h (10^{-3} Pa). Emission spectra recorded using excitation light at 250 (a), 257 (b), and 305 (c) nm.

and its length in several V compounds,³³ a bond length of 1.55 Å is obtained for V species present in C12 V-MCM-41.

For C14 V-MCM-41, the vibrational energy corresponds to 1036 cm^{-1} with a longer V=O bond length (1.56 Å) and a higher symmetry than for the V species present on C12 V-MCM-41. Since the positions of the peak maxima of the vibrational fine structure do not change upon varying the excitation UV wavelength from 250 to 305 nm (Figure 6), the two maxima observed in the excitation spectra at 256 and 302 nm (Figure 2A) are likely related to the same kind of tetrahedral V species.

Discussion

We will first point out the key role of the anti-foaming agent in the preparation of highly ordered hexagonal V-loaded MCM-41 materials. Then we will comment on (i) the role of surface defects in the introduction of V ions in MCM-41 and (ii) the effect of MCM-41 pore size on the symmetry of V species.

Role of the Anti-foaming Agent. When anti-foaming agent is not added to the synthesis solution, XRD patterns vary with the $\text{H}_2\text{O}/\text{Si}$ ratio.^{23b} Addition of an anti-foaming agent improves the reproducibility of V-MCM-41 materials and allows a highly ordered hexagonal MCM-41 structure to form even in an excess of water. It is important to point out that excess water is very helpful for obtaining a more homogeneous synthesis solution, and therefore a better dispersion of V ions in the matrix.^{23b}

Role of Surface Defects in the Introduction of V ions in MCM-41. The present study provides interesting information on (1) photoluminescent properties of siliceous MCM-41 related to surface defects associated with SiO^- and/or SiOH groups, and (2) photoluminescent properties of V-loaded MCM-41 related to surface defects and tetrahedral V species.

The green/blue/violet photoluminescence at 490–400 nm observed for Si-MCM-41 is likely related to SiOH groups, in agreement with Rückschloss et al.^{25,26} who have examined a variety of hydrated metal oxides and attributed green/blue/violet photoluminescence to the presence of M–OH moieties (where M = Al, Si, Zn, or Pb). They have shown that the intensity of this photoluminescence is related to the density of defects with optical absorption in the spectral region $\lambda < 350\text{ nm}$. Similar dependence of the photoluminescence on SiOH content has been observed in various silica glasses²⁸ and VSiβ zeolite,¹² and has been related to the density of structural defects.^{12,28} Two intrinsic defects, peroxy radicals and nonbridging oxygen hole centers (NBOHC), are found most prevalently in silicas with high OH content.⁴⁴ Each of these defects has a characteristic photoluminescence when excited with high-energy photons ($h\nu > 3.5\text{ eV}$): 459 nm for peroxy radical and 620–670 nm for NBOHC. The presence of a third emission band at 425 nm in the photoluminescence spectrum of Si-MCM-41 indicates the possibility of a third form of intrinsic defect in this sample.

Intrinsic defects can be formed in Si-MCM-41 together with SiO^- and/or SiOH, as previously reported for amorphous silica^{27,28,44} and crystalline Siβ zeolite.¹² The presence of some SiO^- groups at the surface of Si-MCM-41 is not surprising since the preparation of this material occurs in a medium ($\text{pH} > \text{IEP}$) favoring the deprotonation of silanol groups.⁴⁵ Thus, not only Si–O–Si (siloxane bridge) and neutral SiOH (silanol) but also SiO^- (siloxo) groups and three types of intrinsic defects can be considered to all be present in Si-MCM-41.

The green/blue/violet photoluminescence at 490–400 nm is also observed for V-MCM-41 samples, and its intensity decreases with increasing content of tetrahedrally coordinated V species. A simultaneous decrease of green/blue/violet photoluminescence intensity and increase of emission intensity of the surface vanadyl groups as a function of V content suggests that the consumption of surface defects and their associated SiO^- and/or SiOH groups takes place upon introduction of V into MCM-41. This consumption is likely to be due to a specific reaction taking place between the vanadium precursor and the surface defects of MCM-41. This clearly illustrates the key role of the defects and their associated silanol groups in the incorporation of vanadium ions in highly ordered MCM-41 materials.

Pore Size Effect on the Symmetry of V Species in MCM-41. The presence of only one kind of tetrahedral V species in C10, C12, and C14 V-MCM-41 indicates that the V ions are very well dispersed in the MCM-41 matrix. The symmetry of tetrahedral V species increases with the pore size. We suggest that this phenomenon is related to the change of the local bond angle of Si–O–V in isolated $(\text{SiO})_3\text{V}=\text{O}$ sites which leads to a change of V=O bond length. Thus, the tetrahedral V species present in C14 V-MCM-41 are less distorted than those present in C12 V-MCM-41 and are characterized by a lower vibrational energy and longer V=O bond.

Finally, photoluminescence spectroscopy allows the detection of surface defects associated with SiO^- and/or SiOH groups in Si-MCM-41, surface defects and tetrahedral V species in C10 V-MCM-41, and tetrahedral V species with different symmetry in C12 and C14 V-MCM-4.

Conclusions

The green/blue/violet photoluminescence at 490–400 nm observed for Si-MCM-41 and V-loaded MCM-41 is likely due to surface defects associated with SiO^- and/or SiOH groups. The simultaneous decrease of green/blue/violet photolumines-

cence intensity with increased emission intensity of the surface vanadyl groups as a function of V content suggests that the surface defects and their associated SiO⁻ and/or SiOH groups disappear upon incorporation of V into MCM-41. Photoluminescence spectroscopy allows one to distinguish, in highly ordered V-loaded MCM-41 materials, only one type of tetrahedral V^V species which is characterized by a specific vibrational fine structure and a short V=O bond length. The local symmetry of vanadium ions dispersed in MCM-41 increases with the pore size of the mesoporous matrix.

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References and Notes

- (1) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; Robert E. Krieger Publishing Co.: Malabar, FL, 1984.
- (2) Chen, C. Y.; Li, H. X.; Davis, M. E. *Microporous Mater.* **1992**, *2*, 17.
- (3) Luan, Z.; Cheng, C. F.; Zhou, W.; Klinowski, J. *J. Phys. Chem.* **1995**, *99*, 1018.
- (4) Pophal, C.; Schnell, R.; Fuess, H. *Stud. Surf. Sci. Catal.* **1997**, *105*, 101.
- (5) Viale, S.; Garonne, E.; Di Renzo, F.; Chiche, B.; Fajula, F. *Stud. Surf. Sci. Catal.* **1997**, *105*, 533.
- (6) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmit, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- (7) Fueston, B. P.; Higgins, J. B. *J. Phys. Chem.* **1994**, *98*, 4459.
- (8) Centi, G.; Perathoner, S.; Trifiro, F.; Aboukais, A.; Aïssi, C. F.; Guelton, M. *J. Phys. Chem.* **1992**, *96*, 2617.
- (9) Sen, T.; Rajamohan, P. R.; Ganapathy, S.; Sivasanker, S. *J. Catal.* **1996**, *163*, 354.
- (10) Moudrakovski, I.; Sayari, A.; Ratcliffe, C. I.; Ripmeester, J. A.; Preston, K. F. *J. Phys. Chem.* **1994**, *98*, 10895.
- (11) Dzwigaj, S.; Peltre, M. J.; Massiani, P.; Davidson, A.; Che, M.; Sen, T.; Sivasanker, S. *J. Chem. Soc., Chem. Commun.* **1998**, 87.
- (12) Dzwigaj, S.; Matsuoka, M.; Anpo, M.; Che, M. *J. Phys. Chem. B* **2000**, *104*, 6012.
- (13) Dzwigaj, S.; Massiani, P.; Davidson, A.; Che, M. *J. Mol. Catal.* **2000**, *155*, 169.
- (14) Schmidt, R.; Akporiaye, D.; Stöcker, M.; Ellestad, O. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1493.
- (15) Yuan, Z. Y.; Liu, S. Q.; Chen, T. H.; Wang, J. Z.; Li, H. X. *J. Chem. Soc., Chem. Commun.* **1995**, 973.
- (16) Das, T. K.; Chaudhari, K.; Chandwadkar, A. J.; Sivasanker, S. *J. Chem. Soc., Chem. Commun.* **1995**, 2495.
- (17) Cheng, C. F.; Klinowski, J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 289.
- (18) Alba, M. D.; Luan, Z.; Klinowski, J. *J. Phys. Chem.* **1996**, *100*, 2178.
- (19) Aguado, J.; Serrano, D. P.; Romero, M. D.; Escola, J. M. *J. Chem. Soc., Chem. Commun.* **1996**, 725.
- (20) Armengol, E.; Cano, M. L.; Corma, A.; Garcia, H.; Navarro, M. T. *J. Chem. Soc., Chem. Commun.* **1995**, 519.
- (21) Corma, A.; Navarro, M. T.; Pariente, J. P. *J. Chem. Soc., Chem. Commun.* **1994**, 147.
- (22) Junger, U.; Jacobs, W.; Martin, I. V.; Krutzsch, B.; Schüth, F. *J. Chem. Soc., Chem. Commun.* **1995**, 2283.
- (23) (a) Wei, D.; Wang, H.; Feng, X.; Chueh, W. T.; Ravikovitch, P.; Lyubovsky, M.; Li, C.; Takeguchi, T.; Haller, G. L. *J. Phys. Chem. B* **1999**, *103*, 2113. (b) Lim, S.; Haller, G. L. Unpublished results. (c) Lim, S.; Haller, G. L. *Appl. Catal. A* **1999**, *188*, 277.
- (24) Gimon-Kinsel, M. E.; Groothuis, K.; Balkus, K. J., Jr. *Microporous Mater.* **1998**, *20*, 67.
- (25) Anpo, M.; Che, M. *Adv. Catal.* **1999**, *44*, 119.
- (26) Patterson, H. H.; Cheng, J.; Despres, S.; Sunamoto, M.; Anpo, M. *J. Phys. Chem.* **1991**, *95*, 8813.
- (27) Rückschloss, M.; Wirschem, Th.; Tamura, H.; Ruhl, G.; Ostwald, J.; Veprek, S. *J. Lumin.* **1995**, *63*, 279.
- (28) Tamura, H.; Rückschloss, M.; Wirschem, Th.; Veprek, S. *Appl. Phys. Lett.* **1995**, *65*, 1537.
- (29) Rückschloss, M.; Ambacher, O.; Veprek, S. *J. Lumin.* **1993**, *57*, 1.
- (30) Jeziorowski, H.; Knözinger, H. *Chem. Phys. Lett.* **1977**, *51*, 519.
- (31) Anpo, M.; Sunamoto, M.; Che, M. *J. Phys. Chem.* **1989**, *93*, 1187.
- (32) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Phys. Chem.* **1980**, *84*, 3440.
- (33) Iwamoto, M.; Furukawa, H.; Matsukami, K.; Takenaka, T.; Kagawa, S. *J. Am. Chem. Soc.* **1983**, *105*, 3719.
- (34) Kazansky, V. B. *Kinet. Katal.* **1983**, *24*, 1338.
- (35) Higashimoto, S.; Zhang, S. G.; Yamashita, H.; Matsumura, Y.; Souma, Y.; Anpo, M. *Chem. Lett.* **1997**, 1127.
- (36) Dzwigaj, S.; Matsuoka, M.; Anpo, M.; Che, M. *J. Phys. Chem. B* **1998**, *102*, 6309.
- (37) Dzwigaj, S.; Matsuoka, M.; Anpo, M.; Che, M. *Catal. Lett.* **2001**, *72*, 211.
- (38) Dzwigaj, S.; Matsuoka, M.; Anpo, M.; Che, M. *Stud. Surf. Sci. Catal.* **2001**, *135*, 356.
- (39) Anpo, M.; Zhang, S. G.; Mishima, H.; Matsuoka, M.; Yamashita, H. *Catal. Today* **1997**, *39*, 159.
- (40) Anpo, M.; Zhang, S. G.; Higashimoto, S.; Matsuoka, M.; Yamashita, H.; Ichihashi, Y.; Matsumura, Y.; Souma, Y. *J. Phys. Chem.* **1999**, *103*, 9295.
- (41) Zhang, S. G.; Higashimoto, S.; Yamashita, H.; Anpo, M. *J. Phys. Chem.* **1998**, *102*, 5590.
- (42) Schraml-Marth, M.; Wokaun, A.; Pohl, M.; Krauss, H. L. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2635.
- (43) Kubokawa, Y.; Anpo, M. *Stud. Surf. Sci. Catal.* **1985**, *21*, 127.
- (44) Munekuni, S.; Yamanaka, T.; Shimogaichi, Y.; Nagasawa, K.; Hama, Y. *J. Appl. Phys.* **1990**, *68*, 1212.
- (45) Parks, G. A. *Chem. Rev.* **1965**, *65*, 177.