Vanadosilicate Mesoporous SBA-15 Molecular Sieves Incorporated with *N*-Alkylphenothiazines

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Received April 18, 2000. Revised Manuscript Received July 25, 2000

Mesoporous silica SBA-15 molecular sieves have been incorporated with various amounts of vanadium via incipient-wetness impregnation with vanadium oxide triisopropoxide in hexane followed by calcination. The products (VSBA-15) have been characterized by nitrogen adsorption and diffuse reflectance UV−visible and electron spin resonance spectroscopies. The results show that the vanadium exists as isolated tetrahedral V^{5+} ions in dehydrated VSBA-15 with $Si/V \geq 40$ while vanadium chains develop as vanadium loading increases. Upon hydration a large fraction of the vanadium is transformed to square pyramidal and distorted octahedral V^{5+} ions by additional coordination to water molecules, suggesting an interior wall surface location for these V^{5+} ions. Upon CO reduction or incorporation of *N*-alkylphenothiazines (PC_n), part of the V^{5+} is reduced to vanadyl VO^{2+} ions. While incorporation of PC_n into VSBA-15 in the dark generates some PC_n^+ cation radicals, ultraviolet photoionization at room temperature further increases the yield for $Si/V = 80$ and 40. The PC_n^+ radicals are more stable in VSBA-15 than in siliceous SBA-15, and the photoyield increases with vanadium loading. The photoyield and stability of PC_n^+ also increase with increasing alkyl chain length of the *N*-alkylphenothiazines.

Introduction

Transition-metal-substituted molecular sieves are of current interest as catalysts for oxidation of a variety of organic compounds where effective but toxic stoichiometric oxidants are used.[1,2] These materials possess uniform pore structure and high surface area and are effective with "clean" and economical oxygen donors such as 30% aqueous hydrogen peroxide.[1−3] Titanium[3,4] and vanadium-substituted silicalites[1,5] are among the most successful materials. Recently, various transition-metal-substituted mesoporous MCM-41 and MCM-48 molecular sieves have also been produced.[6−9] These materials possesses uniform mesopore channels varying from about 15 Å to about 100 Å and have a clear advantage over smaller channel microporous molecular sieves for the adsorption and transformation of large organic molecules.[6−10]

Photoinduced charge separation in various artificial photoredox systems has long been studied for solar energy conversion and storage.[11,12] The charge separation in these systems generally involves a redox reaction between a photosensitive electron donor and a suitable electron acceptor, which generates a pair of radical ions.[13,14] Tremendous effort has been made to extend the lifetime of the photogenerated radical ions in order to exploit the associated energy prior to back electron transfer.[13−19] Generally, long-lived charge separation can be achieved in heterogeneous media such as silica gels[17,18] and zeolites[19] where the radical ion pairs can be sterically separated and molecular mobility is restricted.

SBA-15 is a newly discovered mesoporous silica molecular sieve with uniform tubular channels variable from 50 to 300 Å.[20,21] Incorporation of transition metal ions into SBA-15 by direct hydrothermal synthesis appears unlikely since this mesoporous phase is synthesized in strong acidic media (2 M HCl).[20,21] But

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10.1021/cm000318q CCC: $19.00

transition metal ion incorporation might be achieved by "postsynthesis" grafting involving reaction with a transition metal ion solution.[21−24] We have recently reported such an approach to incorporate titanium[25] or aluminum[21] into SBA-15 as framework species and to prepare thin TiO_2 molecular films anchored inside the mesopores of SBA-15.[25] Here we report a preparation of SBA-15 with incorporated vanadium by reacting SBA-15 with dry hexane solutions of vanadium alkoxide.[24] The products are characterized by nitrogen adsorption and diffuse reflectance UV−visible and electron spin resonance (ESR) spectroscopy. These materials are used as heterogeneous hosts for methylphenothiazine and *N*-alkylphenothiazines which are photosensitive electron donors. Photoionization of these *N*-alkylphenothiazine molecules is achieved at room temperature with 320 nm light.

Experimental Section

Sample. A synthesis procedure for silica SBA-15, designated in this work as SiSBA-15, has been reported.[20,21] Prior to vanadium loading the SiSBA-15 was dehydrated in air at 550 °C for 12 h and then transferred to a glovebox under flowing nitrogen. Vanadium-incorporated SBA-15, designated as VSBA-15, was prepared in a shallow dish inside the glovebox. Vanadium was loaded into SiSBA-15 at room temperature by incipient-wetness impregnation.[24] For every 1 g of SiSBA-15, varying amounts of vanadium oxide triisopropoxide (Aldrich) in 10 g of hexane were used. The vanadium concentration in the solution varies from 0.05 to 0.50 M depending on the desired vanadium loading. The impregnated material was stored in nitrogen at room temperature for 12 h and dried by evaporation in a vacuum. Calcination was performed in air at 550 °C for 5 h. These samples are designated as VSBA-15-(x), where x is the stoichiometric Si/V molar ratio from the incipient-wetness impregnation. For comparison, V_2O_5 powder was used as received from Aldrich.

For CO reduction, VSBA-15 samples were loaded into 3 mm o.d. by 2 mm i.d. Suprasil quartz tubes, evacuated at 425 °C for 2 h, and then exposed to 50 Torr of CO at 200 °C for 2 h. The CO-reduced VSBA-15 samples were flame-sealed for ESR measurement.

Methylphenothiazine was used as received from Aldrich. *N*-Alkylphenothiazines (PC_n, $n = 1, 6, 10, 16$, where n is the number of the carbon atoms in the alkyl chain) were synthesized following a reported procedure.[14,26] PC_n-loaded VSBA-15, designated as PC_n/VSBA-15, was prepared inside a glovebox with flowing nitrogen in the dark. A typical procedure is as follows. Dehydrated VSBA-15 (0.25 g) was immersed in 10 mL of 0.01 M PC_n in benzene for 0.5 h. The benzene solvent was then removed by flowing nitrogen gas directly on the surface of the solution for 2 h. The dried PC_n/VSBA-15 powder was loaded in flowing nitrogen into 3 mm o.d. by 2 mm i.d. Suprasil quartz tubes and sealed with Parafilm for photoionization and ESR measurement.

Photoionization. A Cermax 150 W xenon lamp (ILC-LX150F) was used. The light was passed through a 10 cm water filter and a Corning 7-54 glass filter to give 320 nm irradiation of 1.3×10^6 ergs cm^{-2}/s in the range from 240 to 400 nm.[14,18] Each PC_n/VSBA-15 sample was irradiated in a quartz dewar that was rotated at 4 rpm to ensure even irradiation.

Table 1. Pore Structure Parameters of VSBA-15 Calculated from the Desorption Branch of Nitrogen Adsorption Isotherms Using the Barrett−Joyner−Halenda Formula

materials	A_{BET} ($m^2\,g^{-1}$)	A_{BJH} ($m^2\,g^{-1}$)	V_{BJH} ($cm^3\,g^{-1}$)	D_{BJH} (Å)
SiSBA-15	997	926	1.17	51
VSBA-15-(80)	835	789	1.02	52
VSBA-15-(40)	817	802	1.05	52
VSBA-15-(20)	582	621	0.82	53
VSBA-15-(10)	551	564	0.74	52

Instrumentation. Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics Gemini 2375 analyzer. The volume of adsorbed N_2 was normalized to standard temperature and pressure. Prior to the experiments, samples were dehydrated at 250 °C for 5 h. The specific surface area, A_{BET}, was determined from the linear part of the BET equation ($P/P_0 = 0.05{-}0.31$). Although the Barret−Joyner−Halenda (BJH) analysis underestimates the pore size,[28−31] relative changes in the pore size are accurately portrayed. The calculation of the pore size distribution was performed using the desorption branches of the N_2 adsorption isotherms and the BJH formula.[27] The cumulative pore surface area, A_{BJH}, and volume, V_{BJH}, were obtained from the pore size distribution curves. The average pore diameter, D_{BJH}, was calculated as $4V_{BJH}/A_{BJH}$.

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 200−1000 nm wavelength range against a siliceous SBA-15 standard.

ESR spectra were recorded at X-band at ambient temperature 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 HP 5342A frequency counter.

Results

Nitrogen Adsorption. Characterization of siliceous SiSBA-15 by low-angle X-ray diffraction and nitrogen adsorption has been reported elsewhere,[21,25] which confirms the uniformity of the mesoporous structure (Table 1). VSBA-15 gives similar N_2 adsorption isotherms to that of SiSBA-15 but with decreasing overall N_2 adsorption volume as the vanadium loading increases. Figure 1 shows a typical adsorption isotherm for VSBA-15-(40), which shows an irreversible type IV adsorption isotherm[32] with a sharp inflection in the P/P_0 range from 0.60 to 0.80 characteristic of capillary condensation within uniform pores. A corresponding BJH plot leads to a rather narrow pore size distribution with a pore size of 52 Å (Figure 1, insert). The calculated BET specific surface area is around 1000 m^2/g for SiSBA-15, and it slightly decreases with increasing vanadium loading up to Si/V = 40 (Table 1). Further

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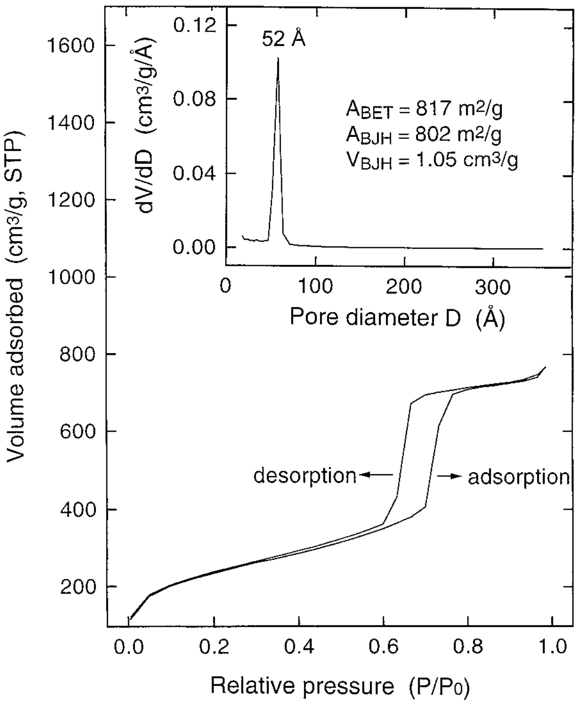

Figure 1. Adsorption isotherms of nitrogen in VSBA-15-(40) at 77 K. The insert shows the corresponding pore size distribution curve.

increase in vanadium loading greatly reduces the BET specific surface area (Table 1). The mesopore surface area A_{BJH} around 900 m^2/g for SiSBA-15 also decreases with vanadium loading. However, the average mesopore diameter, which is about 51 Å for SiSBA-15, remains about the same as the vanadium loading increases up to Si/V = 10 (Table 1). The pore size distributions all look similar for any vanadium loading.

UV–Vis Spectroscopy. Dehydrated VSBA-15 materials are white. At low vanadium loading corresponding to Si/V = 80, VSBA-15 shows only one broad band with a maximum near 270 nm (Figure 2a), which can be assigned to low-energy charge-transfer transitions between tetrahedral oxygen ligands and a central V^{5+} ion.[7,9,33,34] As the vanadium loading increases up to Si/V = 10, the maximum absorption shifts near 300 nm (Figure 2b–d). None of the spectra match that of dehydrated V_2O_5 (Figure 2e) so V_2O_5 does not seem to be formed.

Upon hydration in air the color of VSBA-15 changes rapidly to bright yellow and then orange as reflected by broadening of the UV–vis spectrum toward lower energy (Figure 3). Hydrated VSBA-15 at low vanadium loading gives a band near 370 nm (Figure 3a,b). Further increase in vanadium loading increases the absorption at 370 nm and broadens the spectrum toward lower energy (Figure 3c,d). Repeated dehydration and exposure to hydrated air shows that both the color and UV–vis spectral changes of VSBA-15 are reversible. The VSBA-15 spectra are always different from that of V_2O_5 so V_2O_5 does not seem to be formed.

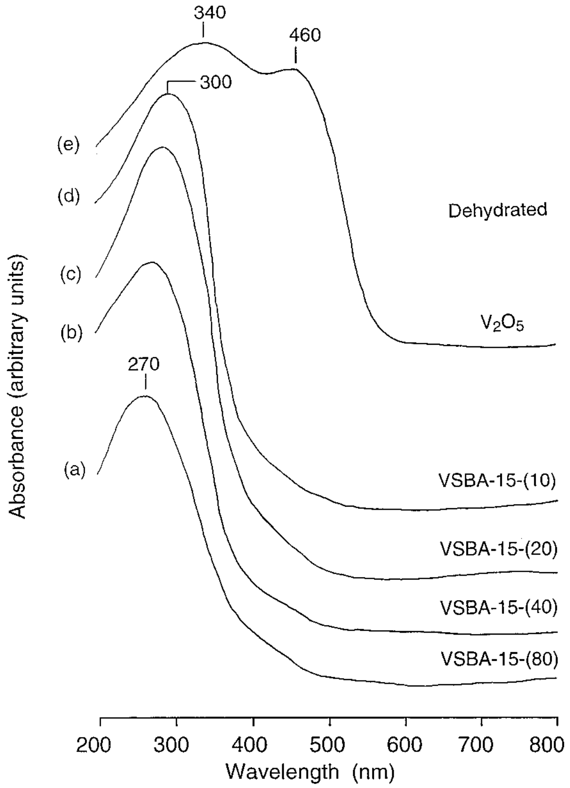

Figure 2. UV–vis spectra (vs siliceous SBA-15) of dehydrated VSBA-15: (a) VSBA-15-(80); (b) VSBA-15-(40); (c) VSBA-15-(20); (d) VSBA-15-(10); (e) V_2O_5.

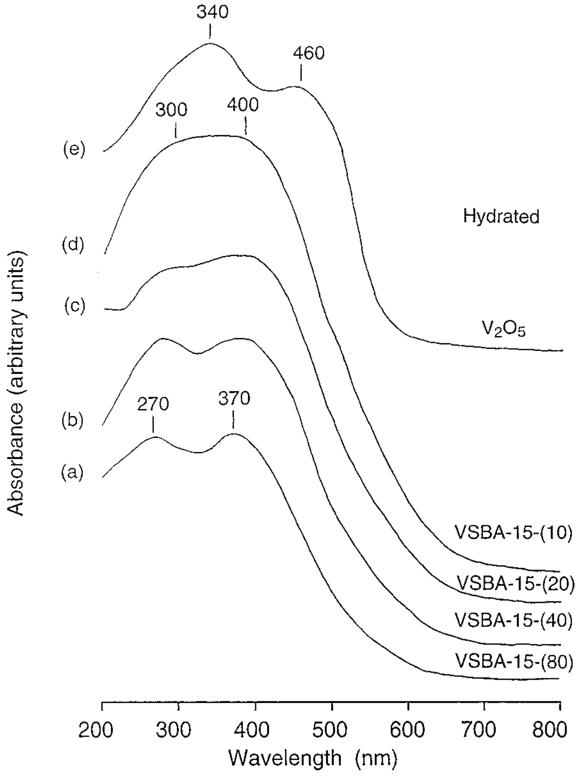

Figure 3. UV–vis spectra (vs siliceous SBA-15) of hydrated VSBA-15: (a) VSBA-15-(80); (b) VSBA-15-(40); (c) VSBA-15-(20); (d) VSBA-15-(10); (e) V_2O_5.

ESR. Freshly prepared VSBA-15 materials give no ESR signals. Following thermal treatment and subsequent CO reduction, all VSBA-15 materials change color from orange to white and then to green and give ESR signals at room temperature as shown in Figure 4. For VSBA-15 with low vanadium loading the ESR spectra

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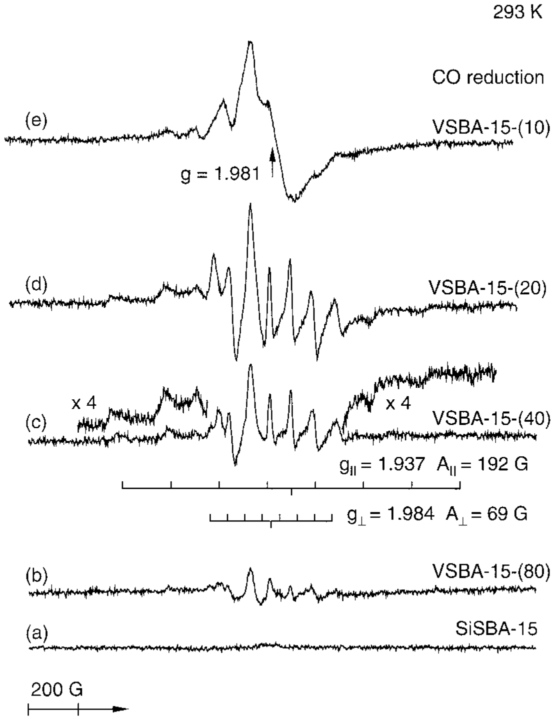

Figure 4. ESR spectra at room temperature of VSBA-15 following CO reduction at 200 °C for 2 h: (a) SiSBA-15; (b) VSBA-15-(80); (c) VSBA-15-(40); (d) VSBA-15-(20); (e) VSBA-15-(10).

(Figure 4b,c) can be characterized by an axially symmetric set of eight lines originating from vanadyl VO^{2+} species coupled to its own nuclear spin (^{51}V, $I_n = 7/2$, natural abundance 99.8%).[35−37] The spin Hamiltonian parameters are $g_{\|} = 1.937$, $A_{\|} = 192$ G, $g_{\perp} = 1.984$, and $A_{\perp} = 69$ G, where A is the hyperfine coupling. At higher vanadium loading, the ESR spectra show reduced resolution of the hyperfine structure (Figure 4d,e).

As shown in Figures 5b,c and 6, incorporation of either methylphenothiazine or *N*-alkylphenothiazines with longer alkyl chains into VSBA-15-(80) and VSBA-15-(40) also generates ESR signals of vanadyl VO^{2+} species in addition to a narrow line at $g = 2.003$ from phenothiazine radical ions (see below). However, the ESR spectra of PC_1/VSBA-15-(20) and PC_1/VSBA-15-(10) with high vanadium loading show mainly VO^{2+} lines (Figure 5 d,e).

Photoionization. Prior to UV irradiation, siliceous PC_1/SiSBA-15 does not give any ESR signal (Figure 5a). In contrast, the PC_1/VSBA-15-(80) and -(40) materials with vanadium indicate a dark reaction as shown by a quite intense line at $g = 2.003$ (Figure 5b,c) which is assigned to methylphenothiazine cation radicals PC_1^{+}.[14,18,38−42] Since the line from PC_1^{+} is overlapped with that from VO^{2+}, a direct measurement of the signal intensity for PC_1^{+} by double integration is not reliable. However, the relative intensity of this line can be estimated from its height, H, defined in Figure 5b. This seems reliable since the $g = 2.003$ is so sharp and intense compared to the multiline VO^{2+} signal. At higher vanadium content with Si/V = 20 this is not so clear so we do not quantitate these systems.

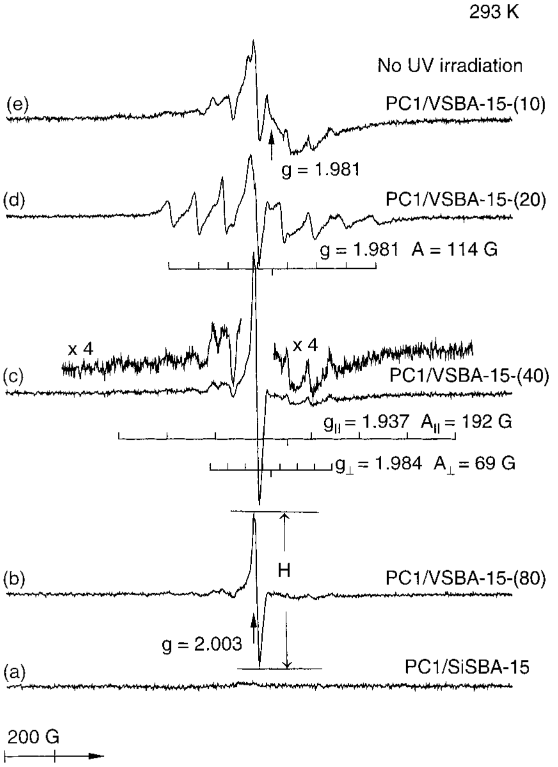

Figure 5. ESR spectra at room temperature of PC_1/VSBA-15 before UV irradiation: (a) PC_1/SiSBA-15; (b) PC_1/VSBA-15-(80); (c) PC_1/VSBA-15-(40); (d) PC_1/VSBA-15-(20); (e) PC_1/VSBA-15-(10).

Following UV irradiation at room temperature the ESR signal intensity H of the line at $g = 2.003$ is also measured at room temperature. The results are given in Figure 7 for both PC_1/SiSBA-15 and PC_1/VSBA-15 materials. The ESR signal of PC_1^{+} increases greatly during the first 10 min and then approaches a plateau. The photoyield is also dependent on the vanadium content in the materials. The ESR signal intensity of PC_1^{+} increases with increasing vanadium content to Si/V = 40. After UV irradiation at room temperature for 60 min, the samples were stored in the dark to allow PC_1^{+} to decay. Figure 8 shows the normalized ESR signal intensities of PC_1^{+} measured at room temperature following the decay as a percentage of the intensity before decay. Figure 8 shows that the PC_1^{+} ESR signal intensity for siliceous PC_1/SiSBA-15 decays relatively rapidly and is reduced to 50% in 1 h and to almost 10% in 10 h. In contrast, the PC_1^{+} ESR signal intensity from PC_1/VSBA-15-(80) and PC_1/VSBA-15-(40) containing vanadium decays significantly slower and may show a decreasing decay rate with increasing vanadium content

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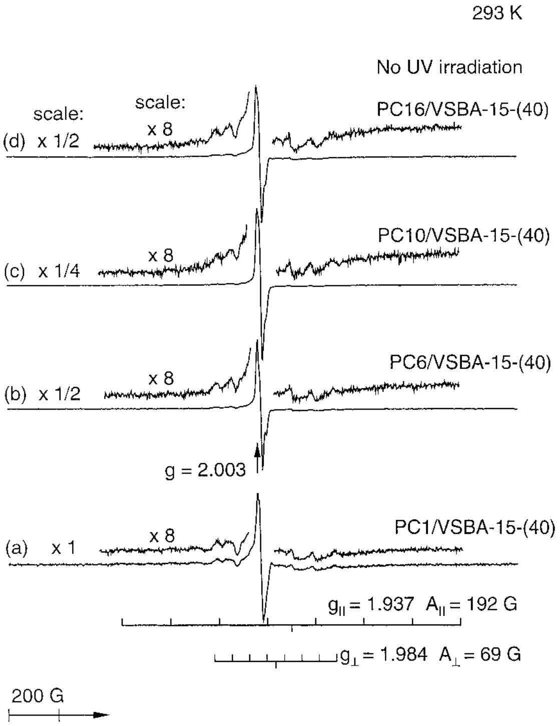

Figure 6. ESR spectra at room temperature of PC$_n$/VSBA-15-(40) before UV irradiation: (a) PC$_1$/SiSBA-15; (b) PC$_6$/VSBA-15-(80); (c) PC$_{10}$/VSBA-15-(40); (d) PC$_{16}$/VSBA-15-(20).

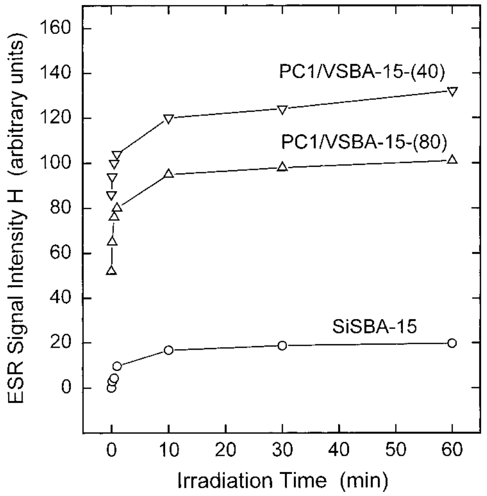

Figure 7. Dependence of the ESR signal intensity of PC$_1^+$ in PC$_1$/VSBA-15 versus irradiation time at room temperature: (○) PC$_1$/SiSBA-15; (△) PC$_1$/VSBA-15-(80); (▽) PC$_1$/VSBA-15-(40); (◇) PC$_1$/VSBA-15-(20); () PC$_1$/VSBA-15-(10).

(Figure 8). After decay for 90 h about 50% of the PC$_1^+$ is still retained for the vanadium materials.

For PC$_n$/VSBA-15-(40) with *N*-alkylphenothiazines having longer alkyl chains, ESR shows a quite intense line prior to UV irradiation (Figure 6). This line at $g = 2.003$ is assigned to *N*-alkylphenothiazine cation radicals PC$_n^+$.[14] The ESR signal intensity *H* of PC$_n^+$ radicals increases with increasing alkyl chain length from methyl ($n = 1$) to decyl ($n = 10$) and then declines with further increase to hexadecyl ($n = 16$) (Figure 6). UV irradiation further increases the yield of PC$_1^+$ and PC$_6^+$ radicals by about 45% but has little effect on the yield for PC$_{10}^+$ and PC$_{16}^+$. As shown in Figure 9, the ESR signal intensity of PC$_n^+$ decays less as the alkyl chain length increases.

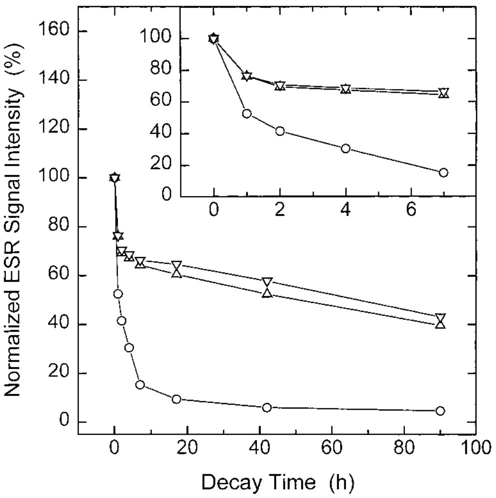

Figure 8. Decay of the ESR signal intensity of PC$_1^+$ in PC$_1$/VSBA-15 at room temperature: (○) PC$_1$/SiSBA-15; (△) PC$_1$/VSBA-15-(80); (▽) PC$_1$/VSBA-15-(40); (◇) PC$_1$/VSBA-15-(20); () PC$_1$/VSBA-15-(10). The insert shows the initial decay period.

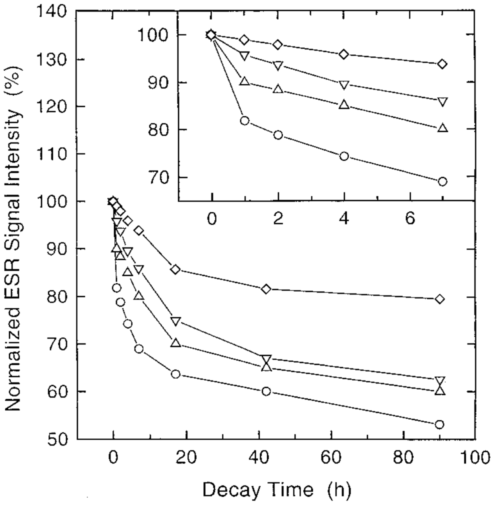

Figure 9. Decay of the ESR signal intensity of PC$_n^+$ radicals in PC$_n$/VSBA-15-(40) at room temperature: (○) PC$_1$/VSBA-15-(40); (△) PC$_6$/VSBA-15-(40); (▽) PC$_{10}$/VSBA-15-(40); (◇) PC$_{16}$/VSBA-15-(40). The insert shows the initial decay period.

Discussion

Pore Structure. As reported earlier,[21,25] siliceous SBA-15 material possesses a narrow pore size distribution with an average pore size of about 51 Å and a high mesopore surface area A_{BJH} of 997 m^2/g (Table 1). Incorporation of vanadium does not much affect the original pore structure of the parent SBA-15 for vanadium loading lower than Si/V = 40 (Figure 1, Table 1). Further increase in vanadium loading reduces the mesopore surface area (Table 1). Since the calculated mesopore diameter remains almost constant (Table 1), the decrease in surface area might be due to pore blocking.

Incorporation of Vanadium. Dehydrated VSBA-15 materials with lower vanadium loading than Si/V = 40 are white and give only one broad UV–vis band with a maximum at 270 nm (Figure 2). Such a band has been extensively reported for various crystalline materials, such as VS-1, VS-2,[1,5,36] VAPO-5,[1,43] and amorphous mesoporous materials[7,9] and has been assigned to colorless tetrahedrally coordinated V^{5+} ions as monomers and is so assigned in this work. Upon CO reduction or incorporation of methylphenothiazine molecules, these VSBA-15 materials with lower vanadium loading give an ESR signal with hyperfine characteristic of vanadyl VO^{2+} ions in square pyramidal coordination (Figures 4 and 5).[1,5,36,43] This along with the color change of VSBA-15 from white to green indicates the reduction of some V^{5+} to VO^{2+} ions. The hyperfine resolution suggests that the VO^{2+} ions are isolated. The UV−vis results support that the vanadium is incorporated into SBA-15 as isolated species for vanadium loading Si/V $\geq$ 40.

Upon hydration, VSBA-15 materials with lower vanadium loading give spectra different from those of corresponding dehydrated materials. A band with a maximum at 370 nm is observed in addition to the 270 nm band seen in dehydrated material (Figure 3). In addition, the color of the materials changes from white to bright yellow and then orange during hydration. It is apparent that a fraction of the vanadium ions is accessible to water molecules and can achieve higher coordination numbers than four upon hydration. This implies that these vanadium ions are coordinated to the interior wall surfaces of SBA-15.

With increasing vanadium loading from Si/V = 40 to 10, the UV−vis spectra of dehydrated VSBA-15 materials show a shift of the maximum of the 270 nm band to near 300 nm but do not match that from dehydrated V_2O_5 (Figure 2). This is similar to reported spectra from various vanadium-containing materials, where a similar band with a maximum near 300 nm has been observed and ascribed to colorless tetrahedrally coordinated V^{5+} ions as chains of tetrahedral vanadia.[36] Upon hydration, UV−vis spectra for Si/V = 20 to 10 show that the band for V^{5+} ions also broadens toward lower energy consistent with increasing coordination with water molecules to become five- and six-coordinated.[7,16,36,37] This previous work also does not suggest the formation of V_2O_5.

Photoionization. PC_1/VSBA-15 materials give a quite intense ESR signal at $g = 2.003$ at room temperature before irradiation (Figure 5). The ESR signal is typical of PC_1^+ as previously reported for PC_1 in homogeneous solution and in silica gels.[38−42] This indicates that some PC_1^+ radicals are produced during the preparation process of the PC_1 /VSBA-15 materials. Ultraviolet irradiation at room temperature generates more PC_1^+ in siliceous PC_1/SiSBA-15 than in PC_1/VSBA-15 materials (Figure 7) which confirms the photooxidation of PC_1 in both siliceous SiSBA-15 and vanado VSBA-15 materials by UV irradiation at room temperature.

For siliceous PC_1/VSBA-15 hydroxyl groups on the wall surfaces[25] might be adsorption sites for PC_1 as well as electron acceptors as has previously been suggested for silica gel materials.[14,18] These hydroxyl groups are weak electron acceptors and cannot induce the oxidation of PC_1 to PC_1^+ without UV irradiation (Figure 5). For PC_1/VSBA-15 materials a second ESR signal of VO^{2+} is observed prior to UV irradiation in addition to the ESR signal of PC_1^+ (Figure 7). Thus, PC_1^+ is apparently generated by interaction with V^{5+} in VSBA-15. Oxidation of PC_1 by V^{5+} seems to be confirmed by the observation that vanadium(V) oxide triisopropoxide in hexane changes color from yellow to light pink upon addition of PC_1 to the solution. The VO^2 and PC_1^+ yields increase with vanadium content up to Si/V = 40.

PC_1^+ generated in SiSBA-15 is relatively unstable at room temperature and decays to about 50% in 1 h and 10% in 10 h (Figure 8), which is comparable to that reported for PC_1^+ in silica gel.[17,18] In comparison, PC_1^+ is more stable in VSBA-15 at room temperature and decays at room temperature by only 50% in several days (Figure 8). This seems related to a higher stability for VO^{2+} and slower back electron transfer to PC_1^+. The slower decay of PC_n^+ with longer alkyl chain lengths is not well understood.

Conclusions

Vanadium has been incorporated into mesoporous silica SBA-15 molecular sieve. Characterization shows that the vanadium is predominantly present as isolated vanadium ions coordinated to the silica walls at vanadium loadings up to Si/V = 40. Incorporation of *N*-alkylphenothiazines into these vanadium containing materials generates *N*-alkylphenothiazine cation radicals, which increase in yield further upon ultraviolet irradiation. The photoyield and stability of the *N*-alkylphenothiazine cation radicals increase with increasing vanadium loading in SBA-15 and with increasing alkyl chain length.

Acknowledgment. This research was supported by the Texas Advanced Research Program, The Environmental Institutute of Houston, and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

CM000318Q

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