

Pseudotetrahedral $\text{O}_{3/2}\text{V}=\text{O}$ Centers Immobilized on the Walls of a Mesoporous, Cubic MCM-48 Support: Preparation, Characterization, and Reactivity toward Water As Investigated by ^{51}V NMR and UV–Vis Spectroscopies

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The high hydroxyl content of mesoporous silicates makes it possible to use them as anchors for the attachment of transition-metal species. In the present study, three different samples corresponding to atomic V/Si ratio of 0.01, 0.05, and 0.10 have been prepared by reacting a silica-based mesoporous matrix of the cubic MCM-48 structure, with dry hexane solutions of $\text{O}=\text{V}(\text{OiPr})_3$. Bulk structural characterization (X-ray diffraction and BET) shows that the cubic structure is maintained during the impregnation process. In the presence of V centers, a noticeable decrease of the main-pore diameter and of the *a* unit-cell parameter is observed. Thus, a strong interaction between the mesoporous walls and the V centers is suggested. The microstructural configuration of V centers has been investigated further by ^{51}V NMR and UV–vis spectroscopies. Both techniques reveal that, in the absence of water, pseudotetrahedral $\text{O}_{3/2}\text{V}=\text{O}$ centers, probably coordinated by three (Si–O–V) bridges, are grafted to the mesoporous walls. The presence of these functional groups and their particular reactivity toward entering ligands such as water impart a number of unique properties to the bulk V/MCM-48, including color changes from white to orange in the presence of moisture.

Introduction

V-zeolites¹ (pore size <10 Å) and V-mesoporous materials² (derived from the silicalite M41S family recently discovered by Mobil researchers³ with pore sizes greater than 20 Å) are remarkable catalysts for the selective oxidation of organic molecules using H_2O_2 as an oxidant. Their large internal surface area (up to 1500 m²/g with mesoporous materials) makes it possible to disperse a large number of catalytically active V centers. In turn, their narrow pore-size distribution instills a high selectivity in their catalytic properties, allowing only molecules able to diffuse into their channels to be transformed. With V-zeolites, catalytic activity is generally limited to molecules with a kinetic diameter lower than ca. 6.5 Å (mainly small alkanes and alkenes). With V-mesoporous materials, however, the transformation of large organic molecules (cycloalkene, cycloalkanes, branched alkanes, for instance) becomes possible. The catalytic potential for this new

class of materials, for example, in the preparation of fine chemicals, is now generating a great deal of interest in their synthesis and characterization.

Despite these potential catalytic applications, only one V-mesoporous material, isomorphous with the hexagonal MCM-41 silicalite described by Mobil³ has been described. Prepared by hydrothermal synthesis, this V-MCM-41 was reported to contain atomically dispersed V centers, incorporated inside the framework of the mesoporous matrix by substitution for Si atoms in regular tetrahedral positions.² This material was found catalytically active for the selective oxidation of cyclododecane. Unfortunately, its array of monodimensional pores could be easily plugged during industrial applications. There is therefore a strong interest in preparing other V-mesoporous materials, isomorphous with the MCM-48 cubic silicalite and characterized by a three-dimensional array of pores. The direct hydrothermal synthesis of such new materials has yet to be reported.

The present paper describes another approach, experimentally easier, making it possible to disperse V active sites on a MCM-48 silicate support. It is known that the walls of mesoporous materials are amorphous and contain a high density of silanol groups (averaged silanol–silanol distance ≈ 7 Å).^{3–5} These hydroxyl groups are used as anchors for the attachment of V sites.

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The impregnation method, derived from the technique used by Yoshida et al.⁶ to disperse V sites on a silica surface, consists of reacting the silanol groups present on the surface of a dehydrated MCM-48 matrix with vanadium alkoxide solutions under an inert atmosphere. Three distinct samples corresponding to atomic V/Si ratios of 0.01, 0.05, and 0.10 are described. Bulk structural characterization techniques (X-ray diffraction and BET) are used to demonstrate that the cubic structure is maintained during the impregnation procedure. The results given by these two techniques are combined to demonstrate that the V species are introduced into the channels of the mesoporous support. Complementarily, ⁵¹V NMR and UV-vis spectroscopies are used to investigate the microstructure of the V centers grafted to the mesoporous walls and their transformation in the presence of water.

Experimental Section

Hydrothermal Synthesis of the MCM-48 Support.

Pure silica MCM-48 was obtained by using a chlorine salt of cetylbenzyltrimethylammonium chloride (CBDA⁺Cl⁻) as a templating agent and tetraethyl orthosilicate (TEOS, Aldrich, Milwaukee, WI) as a silica source. An aqueous solution of surfactant and TEOS was brought to a pH of 11 by addition of NaOH (normalized molar ratio: 1 Si/0.047 surfactant/0.54 NaOH/150 H₂O). The resulting mixture was kept at 100 °C for 10 days in a Teflon flask. Chemical analysis of the white powder obtained gave atomic N/Si ratio and C/N ratio of 0.22 and 0.25, respectively, indicating that the templating agent is not decomposed during the hydrothermal synthesis.

To eliminate the organic cations present inside the mesoporous channels, the above MCM-48 product was heated at a constant heating rate (10 °C/min) up to 500 °C under Ar, then held at 500 °C for 6 h in flowing oxygen. Following the DTA-TGA results presented in refs 3 and 4 during this thermal pretreatment, the organic cations are fully replaced by protons, leaving silanol groups inside the mesoporous channels:



From this stoichiometric mechanism and the chemical analysis performed before heat pretreatment, 22% of the Si atoms present in the final material, labeled calcined MCM-48 hereafter, would be expected to be coordinated to an hydroxyl group.

Impregnation of Vanadium on the MCM-48 Support.

By extension of an impregnation method previously reported for grafting V centers on silica-based matrixes,⁶⁻⁹ we have prepared three samples, referred to as V/MCM-48/0.01, V/MCM-48/0.05, and V/MCM-48/0.10. In these labels, the last value corresponds to the atomic V/Si ratio. A calcined MCM-48 sample, dehydrated under flowing Ar then O₂ for 3 h at 300 °C, was soaked for 1 h in an anhydrous hexane vanadium triisopropoxide (OiPr)₃V=O (Aldrich) solution. Under inert atmosphere (Ar), the obtained powder was filtered, washed twice with anhydrous hexane then calcined at 400 °C under dry O₂ (1 h). Colorless samples obtained in the absence of contact with ambient moisture, are labeled as dehydrated V/MCM-48. Under these conditions, an esterification process between the silanol groups of the mesoporous support and the V precursor, leading to V sites anchored to the walls by one (Si-O-V) bridge, (V sites of type A) is expected.⁶⁻⁹ Multiple esterification processes leading to discrete V centers linked

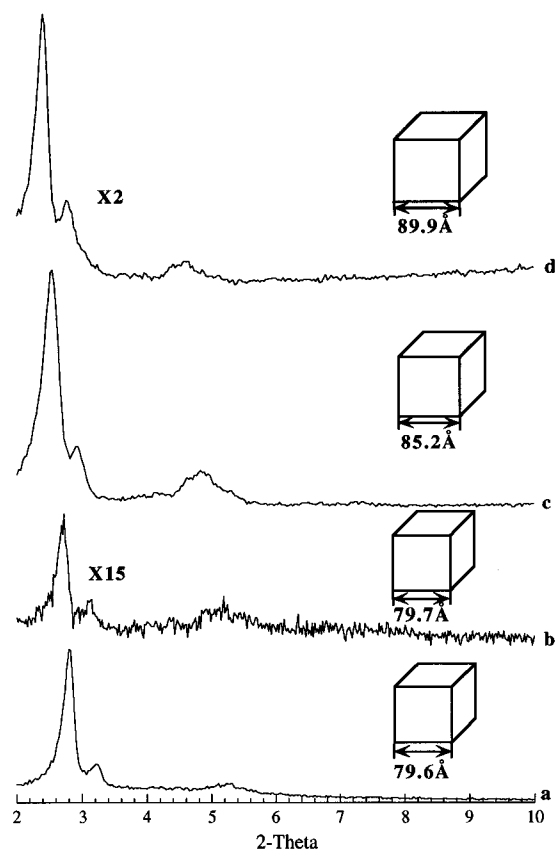


Figure 1. Powder X-ray diffraction patterns of (a) uncalcined (as-made) MCM-48 support, (b) calcined (pore-free) MCM-48 support, (c) dehydrated V/MCM-48/0.05 (sample not contacted with air), and (d) hydrated V/MCM-48/0.05 (after several days of hydration under ambient conditions).

Table 1. Synthesis Conditions, Chemical Analysis, and X-ray Unit-Cell Parameter of the Uncalcined (As-Made) MCM-48, the Calcined (Pore-Free) MCM-48 and the V/MCM-48 Materials

sample	pretreatment	chemical analysis	main pore diam (Å)	$d_{211} \rightarrow a$ (Å)
MCM-48	as-made	N/Si = 0.22 Na/Si < 0.01		36.7 → 89.9
	calcined		25.7	34.8 → 85.2
	hexane			34.8 → 85.2
V/MCM-48/0.01	hydrated	V/Si = 0.01	25	32.2 → 78.9
V/MCM-48/0.05	hydrated	V/Si = 0.06	24	32.5 → 79.6
V/MCM-48/0.10	hydrated	V/Si = 0.12	23	32.4 → 79.4

by two (type B) or three (Si-O-V) bridges (type C) to the mesopore walls are also possible if adjacent silanol groups are present.

Color changes occur immediately if the dehydrated V/MCM-48 samples are exposed to the atmosphere. Subsequent characterizations have then been performed on V/MCM-48 in its dehydrated (colorless material, stored under He after synthesis) and fully hydrated (orange material, obtained after more than 1 day of exposure to moisture under ambient conditions) states. Chemical analyses (Galbraith Laboratories, Inc.) reveal that the actual composition of the hydrated V/MCM-48 materials corresponds to the nominal composition (Table 1), as expected if there is no volatilization of the alkoxide V precursor during thermal treatment.

Characterization Techniques. X-ray powder diffraction patterns (Figure 1) were obtained on a Scintag PADX diffractometer using Cu K α radiation with a liquid nitrogen cooled solid state detector at 45 kV and 40 mA.

N₂ adsorption/desorption isotherms were measured on a Micromeritics ASAP 2000 apparatus. All samples were outgassed initially at room-temperature then at 350 °C until a pressure <1 μ Torr was achieved. The pore size distribution

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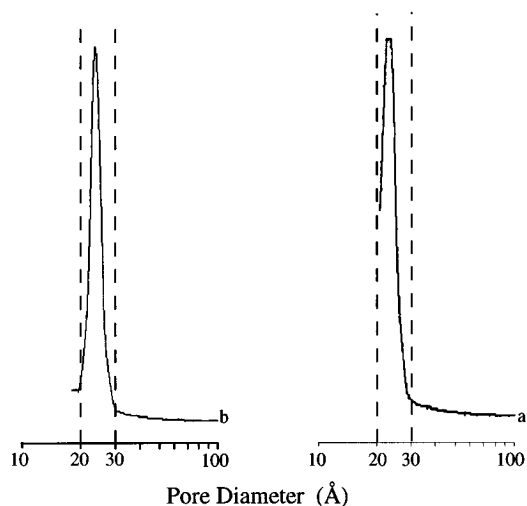


Figure 2. Pore-size distribution in the blank MCM-48 and in the V/MCM-48/0.05 samples (as calculated using BHJ model¹⁰).

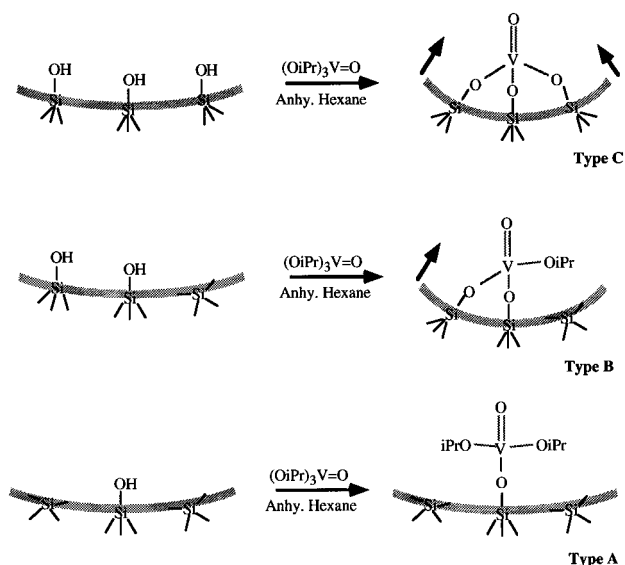


Figure 3. Coordination of V centers on the mesoporous walls. On these scheme, V centers of type B and type C, coordinated by two and three (Si-O-V) bridges to the mesoporous walls, are expected to change the pore curvatures. By contrast, the V centers of type A, only coordinated by one (Si-O-V) bridge to the walls are not expected to change significantly the unit-cell **a** parameter.

presented in Figure 2 and the main pore size summarized in Table 1 were calculated by using the desorption isotherms following the method of Barrett, Joyner, and Halenda (BHJ).¹⁰

Room-temperature solid-state ^{51}V NMR studies were carried out at 79.0 MHz on a General Electric GN-300 spectrometer, equipped with an Explorer high-speed digitizer and a high-speed MAS probe from Doty Scientific. In a typical run 60 000–80 000 scans were accumulated. Wide-line spectra were obtained using a $(\theta - t - 2\theta)$ spin-echo pulse sequence with pulse length of 1 μs , corresponding to $\theta = 45^\circ$ under selective excitation conditions. An echo delay of 50 μs and a relaxation delay of 1 s were used. In all our ^{51}V NMR spectra (Figure 4), as found in many other vanadium containing systems, only the central $[1/2 \rightarrow -1/2]$ transition of the quadrupolar ^{51}V ($I = 7/2$) nucleus is detected. Solid-state ^{51}V NMR spectra are expected to be complex due to the simultaneous presence of second-order quadrupolar effects and chemical shift anisotropy interactions. However, at sufficiently high field

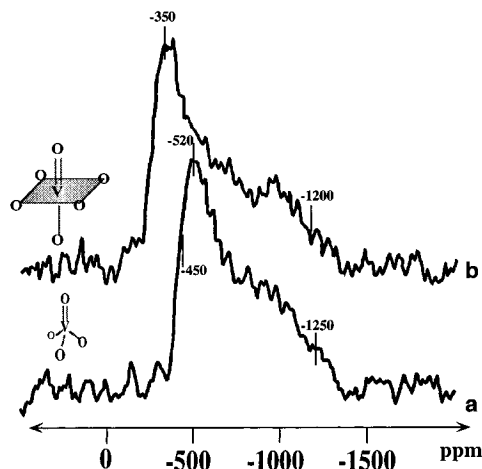


Figure 4. The 79 MHz static ^{51}V NMR spectra of the V/MCM-48/0.1 sample: (a) dehydrated material; (b) hydrated material.

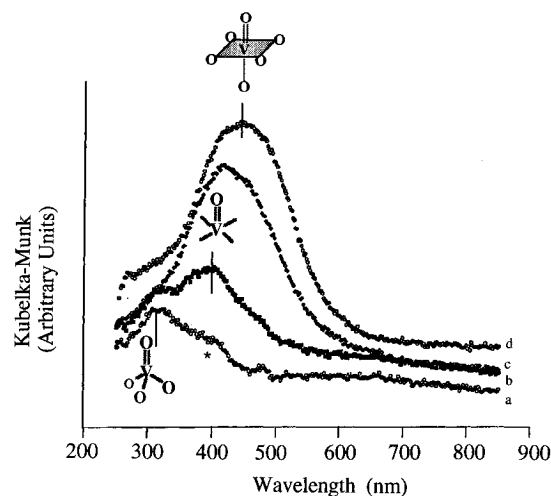


Figure 5. Evolution of UV-vis spectra as a function of hydration time (under ambient conditions) for the V/MCM-48/0.05 sample: (a) time 0; (b) 10 min; (c) 30 min; (d) 2 h.

strengths, the line shapes are dominated by chemical shift anisotropy.^{8,11–13} This also appears to be the case for the present materials, studied at 7.0 T, and approximate values of the δ_{11} , δ_{22} , and δ_{33} principal components of the chemical shift tensor, associated with characteristic singularities of the experimental spectra, are indicated in Figure 4. ^{51}V magic angle spinning NMR spectra were obtained with 45° solid flip angles at variable spinning speeds between 4 and 8 kHz.

The UV-visible diffuse reflectance spectra (Kubelka–Munk units, Figures 5 and 6) were measured with a Cary spectrometer equipped with a reflectance attachment. Reference substances were either dehydrated BaSO_4 , calcined at 300°C for 3 h in an oxygen flow and then cooled under Ar or hydrated BaSO_4 , stored under ambient conditions. A test sample obtained by grinding 10 mg of V_2O_5 (Aldrich) with 200 mg of BaSO_4 is also presented in Figure 6e.

Results and Analysis

Bulk Structural Characterization of the V/MCM-48 Samples. The X-ray diffraction patterns recorded on all the samples (with and without vanadium) match well with those of the silica MCM-48 polymorph re-

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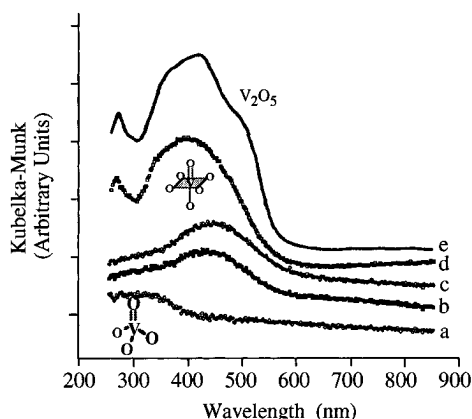


Figure 6. Evolution of UV-vis spectra as a function of hydration time (under ambient conditions) for the V/MCM-48/0.10 sample: (a) time 0; (b) 30 min; (c) 2 h; (d) several days; (e) reference V_2O_5 diluted in $BaSO_4$ sample.

ported by Kresge et al.³ and Monnier et al.⁵ In the cubic $Ia3d$ space group, the two major reflections, (211) and (220), occur within the range $2-3^\circ$ (2θ). The (211) line, easily detected with all the samples, has been used to obtain the approximate unit-cell a parameters reported in Table 1.

Although small uncertainties in low diffraction angle values can lead to nonnegligible variations in d -spacing values, general trends can be observed from these estimates. First, the a unit-cell parameter of the calcined MCM-48 material is smaller than that of the uncalcined MCM-48 (compare Figure 1a and 1b). During the thermal pretreatment used to eliminate the surfactant, hydroxyl groups are formed on the mesoporous walls and a further condensation of the silica matrix can take place.³⁻⁵ The unit-cell a parameter also decreases significantly when hexane (OiPr)₃ V=O solutions are reacted with a dehydrated MCM-48 matrix (compare Figure 1b and 1c). This decrease is not observed for a blank experiment performed by contacting the dehydrated MCM-48 support with hexane in the absence of vanadium. However, as can be seen in Table 1, this decrease is not proportional to the overall vanadium amount. These observations suggest that there are strong interactions between V centers and the silicate walls, a saturation effect occurring at high V concentrations (atomic V/Si ratio >0.01). Furthermore, no noticeable difference has been observed between the X-ray diffraction patterns of the V/MCM-48 samples in their hydrated and dehydrated states (compare Figure 1c and d). The nature of the interaction between the V centers and the silica walls is therefore not strongly affected by moisture exposure.

All the samples give similar adsorption/desorption isotherms of N_2 . The absence of hysteresis indicates a reversible type IV isotherm.¹⁴ A first adsorption step, due to a monolayer adsorption of N_2 on the walls of the mesoporous material, is followed by a sudden increase occurring at $p/p_0 > 0.25$. This increase suggests a large pore volume, and the sharpness of this step reveals uniformity in the pore-size distribution. Figure 2a

depicts the internal pore volume as a function of pore diameter observed for the blank MCM-48 sample. A well-defined peak at 25.7 \AA (full width at half-maximum $\approx 2.5 \text{ \AA}$) indicates a very narrow pore-size distribution. The V/MCM-48 samples exhibit a similar pore-size distribution but slightly broadened (V/MCM-48/0.05 characterized by a main pore size of 24 \AA and a full width at half-maximum $\approx 4 \text{ \AA}$, for instance).

To summarize, the bulk characteristics of the V/MCM-48 samples are comparable but not identical to those of the calcined MCM-48 support. As indicated by X-ray diffraction, the cubic structure is preserved after V impregnation. BET also reveals that, in the presence of vanadium, the mesoporous channels remain accessible. Their main-pore diameter decreases significantly, however (Table 1, Figure 2, main pore size decrease of $\approx 10\%$). This last observation suggests that V species are located inside the channels, coating the walls of the mesoporous matrix. Finally, a significant decrease (7% for an atomic V/Si ratio of 0.10) of the unit-cell parameter a is observed after vanadium introduction and indicates strong interactions between the V centers and the mesoporous walls. The presence of oxovanadium functional groups, multiply coordinated via (Si-O-V) bridges to the walls, could explain this last observation. Indeed, some pore-size shrinking, associated with a unit-cell decrease could be expected if the V species are bonded to two (type B) and/or three (type C) Si-O groups and tend to curve the silica walls, as schematically indicated in Figure 3.

UV-Vis and ^{51}V NMR Spectroscopic Characterizations. The coordination of V centers in the V/MCM-48 materials was probed directly by ^{51}V NMR. Since the NMR spectral features are not drastically affected by the overall vanadium content, only the spectra with the highest signal-to-noise ratio, obtained with the V/MCM-48/0.10 sample in its dehydrated and hydrated states are presented in Figure 4a,b. The spectrum of the dehydrated V/MCM-48/0.10 is characterized by a near-axially symmetric shift tensor with principal components near -450 , -520 , and -1250 ppm vs VOCl_3 . These values are to be considered averages due to a distribution of local V environments. The distribution effect is particularly apparent for the δ_{33} component near -1250 ppm , corresponding to the shielding along the V=O double bond. This observation suggests that a range of V=O bond lengths exists in this material, possibly due to intermolecular interactions with hydroxyl groups. Previous studies of discrete vanadium compounds with well-characterized local environments^{8,13,15} have shown that the anisotropic chemical shift parameters of the ^{51}V nucleus are highly diagnostic of its coordination geometry. As can be seen from the literature data summarized in Table 2, ^{51}V NMR spectroscopy discriminates well between octahedral and tetrahedral distorted vanadium species. Distorted octahedral V species are associated with a δ_{22} value in the range $-200/-400 \text{ ppm}$ while distorted tetrahedral V species are associated with more negative δ_{22} values (within the range $-450/-550 \text{ ppm}$). Inspection of the ^{51}V chemical shift database^{8,11,13,15} reveals that the spectrum in Figure 4a is in excellent agreement (in terms of asymmetry and of δ_{ij} values) with those

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Table 2. ^{51}V NMR Parameters of Various V^{V} -Containing Materials^a

ref	compound	δ_{11}	δ_{22}	δ_{33}	coordn
15	NaVO_3	-360	-530	-840	distorted tetrahedral $\text{O}_{2/2}\text{VO}^-$
15	NH_4VO_3	-370	-530	-830	
8	$(\text{Ph}_3\text{SiO})_3\text{V}=\text{O}$	-510	-525	-1150	
8	$[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{V}=\text{O}]_2$	-500	-535	-1115	
8	0.05 molar V/SiO_2 (dehydrated)	-450	-470	-1190	pseudo-tetrahedral $\text{O}_{3/2}\text{VO}$
17	0.005 molar V/SiO_2 (dehydrated) ^b	-450	-520	-1250	
tw	$\text{V}/\text{MCM-48}/0.10$ (dehydrated)	-450	-520	-1250	
15	V_2O_5	-280	-280	-1250	
8	0.05 molar V/SiO_2 (hydrated) ^c	-250	-330	-1200	distorted octahedral
17	0.005 molar V/SiO_2 (hydrated) ^b	-350	not det.	not det.	
tw	$\text{V}/\text{MCM-48}/0.10$ (hydrated)	-350	-350	-1200	

^a δ_{ii} ($i = 1, 2, 3$) values in ppm expressed relative to VOCl_3 ; tw, this work. ^b Nanocomposite material obtained by sol-gel chemistry. ^c Obtained by impregnation of $\text{O}=\text{V}(\text{O}-i\text{-Pr})_3$ on a pure silica support (fumed Cab-O-Sil).

reported for various silsesquioxane model compounds $\{(\text{Ph}_3\text{SiO})_3\text{V}=\text{O}$ and $[(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})\text{V}=\text{O}]_2\}$.⁸ According to X-ray crystallographic data,¹⁶ in both model compounds the coordination of V centers is composed of one $\text{V}=\text{O}$ double bond and three $\text{V}-\text{O}-\text{Si}$ bridges. Similar spectral features have also been reported for vanadium species sequestered into a silica gel¹⁷ and for V centers immobilized on a dehydrated SiO_2 surface.⁸ In the last case, detailed EXAFS/XANES,⁶ Raman,^{7,8} and ^{51}V NMR studies^{8,9} have clearly identified a pseudotetrahedral $\text{O}_{3/2}\text{V}=\text{O}$ coordination environment, with V centers coordinated by three $(\text{Si}-\text{O}-\text{V})$ bridges to the silica support. All the other known coordination environments are characterized by substantially different chemical shift tensor values (Table 2). We conclude then that the V centers present in the dehydrated $\text{V}/\text{MCM-48}/0.10$ sample are mainly pseudotetrahedral $\text{O}_{3/2}\text{V}=\text{O}$ species, probably coordinated by three $(\text{Si}-\text{O}-\text{V})$ to the mesoporous walls.

Figure 4b shows the ^{51}V NMR spectrum of the same sample ($\text{V}/\text{MCM-48}/0.10$) in its fully hydrated state. After 2 days of hydration, only an axially symmetric site with principal components located at -350 and -1200 ppm vs VOCl_3 can be detected. These features are characteristic of V species in a distorted octahedral ligand field, illustrating that dramatic changes occur in the vanadium coordination sphere upon exposure to moisture. Very similar spectra have been reported for vanadia two-dimensional deposits (monolayer) overlaying a hydrated silica surface.⁸ Likewise, hydration of vanadium species dispersed into SiO_2 gels results in similar spectral features, although in that case not all the $\text{O}_{3/2}\text{V}=\text{O}$ centers are accessible for entering water ligands.¹⁷ By contrast, the absence of any clear contribution within the range -500 to -550 ppm for the hydrated $\text{V}/\text{MCM-48}/0.10$ sample (Figure 4b) demonstrates that in the $\text{V}/\text{MCM-48}$ materials all the $\text{O}_{3/2}\text{V}=\text{O}$ centers are accessible to water. MAS-NMR studies reveal a well defined spinning sideband pattern cen-

tered at -585 ppm and extending over the frequency range of the static spectrum. These results confirm the close structural similarity of these octahedral vanadium sites with those observed on the hydrated silica surface.⁸ Furthermore, there are no indications that the ability of MAS to refocus transverse magnetization is affected by molecular tumbling on the NMR time scale (10^{-4} s). Thus, both the static and MAS NMR line shapes are consistent with vanadium moieties that are, from the NMR point of view, rigid at room temperature.

In summary, these ^{51}V NMR results suggest that on the dehydrated MCM-48 surface $\text{O}_{3/2}\text{V}=\text{O}$ pseudotetrahedral species are formed, which are converted to octahedral species by direct coordination of water molecules. The chemical shift parameters and the reversible changes observed upon hydration unambiguously differentiate these $\text{O}_{3/2}\text{V}=\text{O}$ sites from bulk V_2O_5 . Thus, ^{51}V NMR provides detailed information about the microstructure of the V centers present in the $\text{V}/\text{MCM-48}$ materials in their dehydrated and fully hydrated states. However, water coordination is a very rapid phenomenon (as indicated by the color change immediately visible upon moisture exposure), and long accumulation times are required for high-quality ^{51}V NMR spectra so that it is not possible to follow the water coordination process by NMR. In situ information should prove useful and has been checked by UV-vis spectroscopy.

For oxoanions of V^{V} (electronic configuration $3d^0$), very strong absorptions due to charge-transfer (CT) transitions between oxygen ligands and the central V atoms are generally observed in the UV-vis region.¹⁸ The value of these electronic CT energies are strongly influenced by the local structure of V sites and by the size of the V domains investigated. Isolated species generally give rise to CT transitions in a higher energy range than polymeric species (the well-established blue-shift of semiconductor particles, a function of size effects). Some data available from the literature^{1b,17-19} regarding the correlation between the coordination sphere of V sites and their characteristic UV-vis features are summarized below and in Table 3.

For $\text{O}_{3/2}\text{V}=\text{O}$ pseudotetrahedral species deposited on a dehydrated silica surface, only one broad CT transition located below 350 nm has been observed.¹⁹ In more symmetric materials, in which vanadium is surrounded by four nearly equivalent oxygen ligands (NH_4VO_3 , K_3VO_4 , Ti_3VO_4 , or Na_3VO_4), a first (lower) charge-transfer transition (LCT), attributed to a $\pi(t_1) \rightarrow d(e)$ transition, is found below 350 nm and is associated with a second CT within the range 260-280 nm, assigned to a $\pi(t_2) \rightarrow d(e)$ transition.^{1b} For V species in a square-pyramidal coordination sphere, a main CT transition near 400-415 nm is generally observed. In V_2O_5 , the vanadium environment consists of four equatorial $\text{V}-\text{O}$ bonds of similar length (mean $\text{V}-\text{O}$ distance of 1.8 Å), an axial very long and an axial very short $\text{V}=\text{O}$ bond (2.78 and 1.58 Å). This distorted octahedral coordination leads

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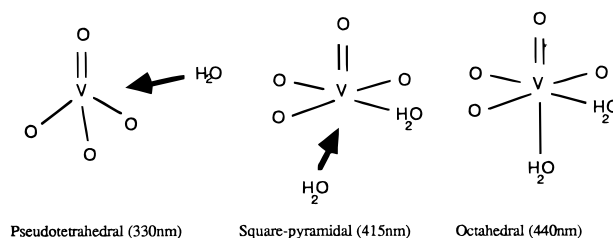
Table 3. UV–Vis Patterns of Various V^V-Containing Materials

compounds	sym	O → M (CT) transitions (nm)	ref.
K ₃ VO ₄ , Ti ₃ VO ₄	isolated distorted tetrahedral VO ₄ ³⁻	$\pi(t_1) \rightarrow d(e)$, 330	19
NH ₄ VO ₃	polymeric distorted tetrahedral O _{2/2} VO ₂ ⁻	$\pi(t_2) \rightarrow d(e)$, 260 $\pi(t_1) \rightarrow d(e)$, 330	19
V/SiO ₂ (dehydrated)	pseudotetrahedral O _{3/2} V=O	$\pi(t_2) \rightarrow d(e)$, 270 <350 (broad)	20
V/MCM-48 (dehydrated)		<350 (broad)	(tw)
V/SiO ₂ (hydrated)	distorted octahedral	450 (broad)	20
V/MCM-48/0.10 (hydrated)	distorted octahedral	440 (broad)	(tw)
V ₂ O ₅	distorted octahedral	$\pi(e) \rightarrow b_2(xy)$, 402 $\pi(a_1) \rightarrow b_2(xy)$, 322 $\pi(b_1) \rightarrow b_2(xy)$, 260 $\pi(e) \rightarrow b_2(xy)$, 400	(tw)
V/MCM-48/0.10 (hydrated)	distorted octahedral	$\pi(a_1) \rightarrow b_2(xy)$, 322 $\pi(b_1) \rightarrow b_2(xy)$, 260	(tw)

to three main CT absorptions occurring at 260, 330, and 402 nm. On the basis of Jorgensen's assignments,²⁰ the most intense transition (402 nm) can be attributed to the $e(\pi) \rightarrow b_2(xy)$ transition involving mainly the axial oxygen atom doubly bonded to the vanadium atom, whereas the two transitions observed at 260 and 330 nm can be associated respectively with the $a_2(\pi) \rightarrow b_2(xy)$ and $b_1(\pi) \rightarrow b_2(xy)$ transitions involving the four equatorial oxygen containing ligands. Recently, an additional transition located near 485 nm has been reported for bulk vanadia and assigned, because of its position (lower in energy than the CT for V=O groups), to an electronic transition between oxygen atoms and a delocalized acceptor level.^{1b} This band reveals the presence of conjugated octahedral sites, i.e., the presence of V–O–V linkages. Finally, in very distorted octahedral environments, for hydrated V/SiO₂¹⁹ (Aerosil materials, for instance), a broad CT transition at 450 nm has been reported.

On the basis of these literature values, the UV–vis spectra of the dehydrated V/MCM-48 materials (Figures 5a and 6a) which show only one broad component at 325 ± 10 nm, are unique and indicate O_{3/2}V=O groups in a pseudotetrahedral ligand field. To study the evolution of these V centers during hydration, we have measured the UV–vis spectra of the V/MCM-48 materials as a function of time, the UV–vis cell being quickly opened to ambient conditions at time zero. The spectral changes observed for low vanadium loadings (V/MCM-48/0.01 and V/MCM-48/0.05 samples) are similar. The spectra collected with the V/MCM-48/0.05 are presented in Figure 5. After 10 min of air exposure, the intensity of the 315 nm band, characteristic of the O_{3/2}V=O centers decreases while a low-energy band at 415 nm progressively emerges. After 30 min, the 315 nm band vanishes, the intensity of the 415 nm band decreases, and a new band at 440 nm appears. After 2 h of air exposure, no more spectral changes are observed and only the 440 nm band remains even after several weeks. The tendency of isolated pseudotetrahedral V^V compounds to increase their coordination sphere either by adding water ligands or through oligomerization process is well documented, as are the associated color changes.²¹

The spectral changes observed here suggest that a direct coordination of water molecules to the vanadium metal centers converts the pseudotetrahedral environment of O_{3/2}V=O centers to one of higher coordination number; bands at 415 and 440 nm being respectively associated to square-pyramidal and octahedral ligand fields:



A similar evolution is observed with the vanadium-rich V/MCM-48/0.10 sample. One broad band at 335 nm is observed in the absence of water, and the maximum of absorbance is shifted to a lower energy value when water is admitted inside the UV–vis cell. After 2 h of air exposure, only one broad absorption at 430 nm is detected. The spectrum continues to change and after a 24 h period the stable signal presented in Figure 6d is obtained. At that stage, three main absorptions at 260, 335, and 400 nm are observed. These band positions, similar to the one reported for bulk vanadia (260, 330, and 402 nm; see the reference spectrum given in Figure 6e) suggest an oligomerization of the vanadium species.

Using UV–vis spectroscopy, we have also checked whether the coordination of water to V centers is reversible or not. A heat pretreatment at 200 °C under flowing O₂ returns the orange hydrated V/MCM-48/0.05 material to its white original color. Spectral features similar to the one presented in Figure 5 are observed even after multiple (five) cycles of hydration/dehydration.

Discussion

Bulk structural characterization techniques (X-ray diffraction, BET) give information about the mesoporous matrix itself, before and after the V impregnation. The calcined MCM-48 support and the V/MCM-48 samples are similar but not identical. The main pore size and the *a* unit-cell parameter are significantly decreased after V introduction, as can be expected if the V centers are coordinated by more than one Si–O–V bridge to the mesoporous walls, thus pulling the pore walls inward.

Local information about the coordination sphere of the vanadium species has been obtained by ⁵¹V NMR and UV–vis spectroscopy. In dehydrated V/MCM-48 samples, both techniques indicate a unique O_{3/2}V=O coordination environment, very similar to that previously reported for V species grafted by 3(Si–O–V) bridges to the surface of a dehydrated silica support (on the basis of ⁵¹V NMR studies⁸ and of fluorescence spectra²¹). Both techniques also demonstrate that all the O_{3/2}V=O groups are easily accessible and react with water to generate distorted octahedral vanadium spe-

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cies. Since it is well-known²² that, in the presence of water, pseudotetrahedral $O_{3/2}V=O$ species increase their coordination sphere either by adding water ligands or via oligomerization processes, in the hydrated V/MCM-48 samples the nature of the V coordination sphere in terms of V–OH, V–OH₂, V–O–V, and Si–O–V bonds is difficult to determine precisely. However, we suggest that (Si–O–V) bridges remain in hydrated V/MCM-48 materials for the following three reasons. First, X-ray diffraction fails to detect any clear difference between hydrated and dehydrated V/MCM-48 materials though some structural relaxation could be expected if, during hydration, the $O_{3/2}V=O$ centers were disconnected from the mesoporous walls. Secondly, hydration/dehydration is fully reversible, and ⁵¹V NMR and X-ray diffraction fail to detect any bulk V₂O₅ domains in the hydrated V/MCM-48/0.10 sample. Finally, BET measurements reveal that after hydration, the mesoporous channels are still accessible, as can be expected if V species were still grafted to the mesoporous walls.

UV–vis spectroscopy also reveals that during water adsorption, the evolution of the V centers is a function of the overall vanadium amount. On one hand, in the V/MCM-48/0.01 and V/MCM-48/0.05 samples containing small amounts of vanadium, the hydration of isolated $O_{3/2}V=O$ groups gives mainly octahedral V species characterized by the broad CT band near 440 nm. On the other hand, the vicinal $O_{3/2}V=O$ groups mainly present in the V/MCM-48/0.10 sample, first react with water to give hydrated octahedral species (broad absorption band at 430 nm observed after 2 h of hydration). In a second step, these hydrated species oligomerize, as indicated by the three CT bands located at 260, 340, and 400 nm observed after 24 h of hydration, similar to that observed with bulk vanadia. Nevertheless, the strong absorption present at 485 nm for bulk vanadia (Figure 6e), which is considered as a fingerprint for the presence of V–O–V linkages^{1b}, remains very weak for the hydrated V/MCM-48/0.10 sample (compare Figure 6d and 6e). This result suggests that the V···O···V interaction in these V/MCM-48 materials is significantly different than in bulk vanadium oxide.

Conclusions

The present study demonstrates that ultralarge-pore materials containing highly dispersed V centers and having a cubic MCM-48 structure can be synthesized by grafting. Combined spectroscopic (UV–vis and ⁵¹V NMR) and bulk structural characterizations (X-ray diffraction, BET) show that pseudotetrahedral $O_{3/2}V=O$ species, with three basal oxygen atoms (belonging either to V–OH or V–O–Si bonds) are formed by reacting V alkoxide precursors with the silanol groups present inside the MCM-48 pores. These oxovanadium(V) species are easily accessible and coordinate to small entering ligands, such as water. Since V species coating the external surface of substrates such as bulk titania or silica are known to act as powerful oxidation catalysts, this new class of V/MCM-48 materials is potentially of

interest. However, in conjunction with testing their catalytic behavior, the following fundamental questions might be addressed:

(i) In the experimental conditions described here (heating treatment under flowing O₂ and temperatures lower than 450 °C), only pentavalent vanadium species have been identified. Changing the vanadium oxidation state might modify the connectivity between the V species and the MCM-48 support. Reduction might also alter their ability to reversibly coordinate entering ligands. However, a previous ESR study, using carbon monoxide and third-derivative ESR spectra to probe vanadium(IV) coordination vacancies, has shown that surface vanadium(IV) species on reduced V₂O₅/SiO₂ catalysts have a pseudotetrahedral $O_{3/2}V=O^-$ coordination.²³ A pseudotetrahedral coordination has also been found for reduced molybdenum(V) species on thermally reduced silica-supported catalysts, and in that case a reversible coordination of water was possible.²⁴ To check if these results can be extrapolated to the vanadium(IV) sites present in reduced V/MCM-48 materials, a detailed ESR study should prove useful.

(ii) The surface chemistry of silica-based materials is dominated by the presence of different types of surface silanol groups. On amorphous silica for instance, isolated, vicinal (H-bonded) and geminal silanols have been identified by infrared and NMR studies.²⁵ A distribution of silanol species is also present on the mesoporous walls of a MCM-41 silica-based material, as described recently.²⁶ By extension, one crucial and unanswered question is then what kind of silanol groups are present on the mesoporous walls of the MCM-48 support before vanadium introduction. The nature and the connectivity between these silanol groups is very likely a critical parameter in determining the final dispersion of the vanadium sites. Thus, optimization of the methodology for preparing mesoporous materials with good physicochemical characteristics and highly accessible hydroxyl groups is currently in progress in our laboratories.

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