

Synthesis of Stable, Hydrophobic MCM-48/ VO_x Catalysts Using Alkylchlorosilanes as Coupling Agents for the Molecular Designed Dispersion of $\text{VO}(\text{acac})_2$

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The use of dimethyldichlorosilane as a coupling agent for the grafting of VO_x structures on the MCM-48 surface produces a material that is simultaneously hydrophobic (immiscible with water) and very active (all V centers are accessible, even for water molecules). The VO_x surface species are grafted by the molecular designed dispersion of $\text{VO}(\text{acac})_2$ on the silylated surface, followed by a calcination in air at 450 °C. These hydrophobic MCM-48 supported VO_x catalysts are thermally stable up to 500 °C. The grafted VO_x surface species are very resistant toward leaching-out in aqueous media. Also, the structural and hydrothermal stability has improved enormously. The crystallinity of the materials does not decrease when the samples are subjected to a hydrothermal treatment at 150 °C and 4.7 atm pressure. A reaction mechanism is proposed and consolidated by FT-IR, Raman spectroscopy, and UV–vis diffuse reflectance. Pore size distributions, water adsorption isotherms, and X-ray diffractograms confirm the structural stability of these materials.

Introduction

The discovery of MCM materials has expanded significantly the possibilities for processing bulky molecules for catalytic and adsorption purposes.^{1,2} In the early years (1992–1996), the main emphasis was on the optimization of the synthesis of the MCM materials. Especially the reproducible synthesis of MCM-48 has been an important difficulty. In the past few years, several research groups, including ourselves,³ have found elegant ways to synthesize high-quality MCM-48. Moreover, several research groups have reported lately on the successful activation of these mesoporous, semicrystalline silica zeolites, either by hydrothermal incorporation of active heteroelements or by surface grafting.⁴

However, three major drawbacks still limit the use of such materials on a large scale: (1) the burning out of the surfactants imposes large economic and ecological disadvantages; (2) the stability in hydrothermal conditions or at higher temperatures needs to be improved; (3) incorporated and/or grafted transition metal ions leach out of the structure in aqueous solutions.

The first drawback can be ruled out by extraction and subsequent recovery and recrystallization of the surfactant. Most successful extractions were performed on mesoporous zeolites, prepared by the so-called S^0T^0 mechanism, i.e., neutral amines are used as surfactants. The weak assembly, due to hydrogen bonding, facilitates the surfactant extraction.⁵ However, some studies have been reported on the (partially) successful extraction of cationic surfactants⁶ and we are able now to recuperate more than 90% of the original Gemini surfactant.⁷

This paper deals with the two other problems. It is generally agreed that the instability of the MCM structures is caused by water attack, breaking some siloxane bonds of the relatively thin silica wall, causing in the end a complete destruction of the ordered porous structure. The second problem is that most

transition metals interact only weakly with a pure silica surface and will therefore leach out easily, especially in aqueous media.^{8,9}

Some researchers have tried to stabilize the MCM wall by a complete hydrofobization of the surface, replacing every silanol group with a trimethylsilyl group, using, e.g., trimethylchlorosilane or hexamethyldisilazane.^{10–12} Although this treatment is very effective in se, it yields a surface that is completely unreactive toward subsequent grafting of transition metals.

We present an approach of selective, partial hydrofobization of the silica walls, using dimethyldichlorosilane, rendering it essentially hydrophobic to withstand the water attack but creating simultaneously sufficient active sites for a subsequent grafting of the surface.

Experimental Section

Pure silica MCM-48 was prepared using the gemini 16–12–16 surfactant (general formula $[\text{C}_n\text{H}_{2n+1}\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_s-\text{N}^+(\text{CH}_3)_2\text{C}_m\text{H}_{2m+1}]\text{Br}$), as described previously.³ The material was silylated using appropriate amounts of $\text{Cl}_2\text{Si}(\text{CH}_3)_2$ (dimethyldichlorosilane, DMDCS) and $\text{N}(\text{C}_2\text{H}_5)_3$, dissolved in toluene. After filtration and vacuum-drying at 300 °C, the silylated MCM-48 was hydrolyzed by stirring in water for 2 h and dried at 300 °C in a regular furnace. $\text{VO}(\text{acac})_2$ was anchored on the silylated surface using the gas-phase molecular designed dispersion method.¹⁵ Finally, the sample was calcined at 450 °C.

Infrared spectra were measured on a Nicolet 5DBX spectrometer, equipped with a MTEC photoacoustic detector. X-ray diffractograms were recorded on a Philips PW1840 powder diffractometer, using Ni-filtered $\text{Cu K}\alpha$ radiation. Porosity and surface area studies were performed on a Quantachrome Autosorb-1-MP automated gas adsorption system. The calcined samples were degassed for 17 h at 200 °C. Gas adsorption occurred using nitrogen as the adsorbate at liquid nitrogen temperature. Surface areas were calculated using the well-known

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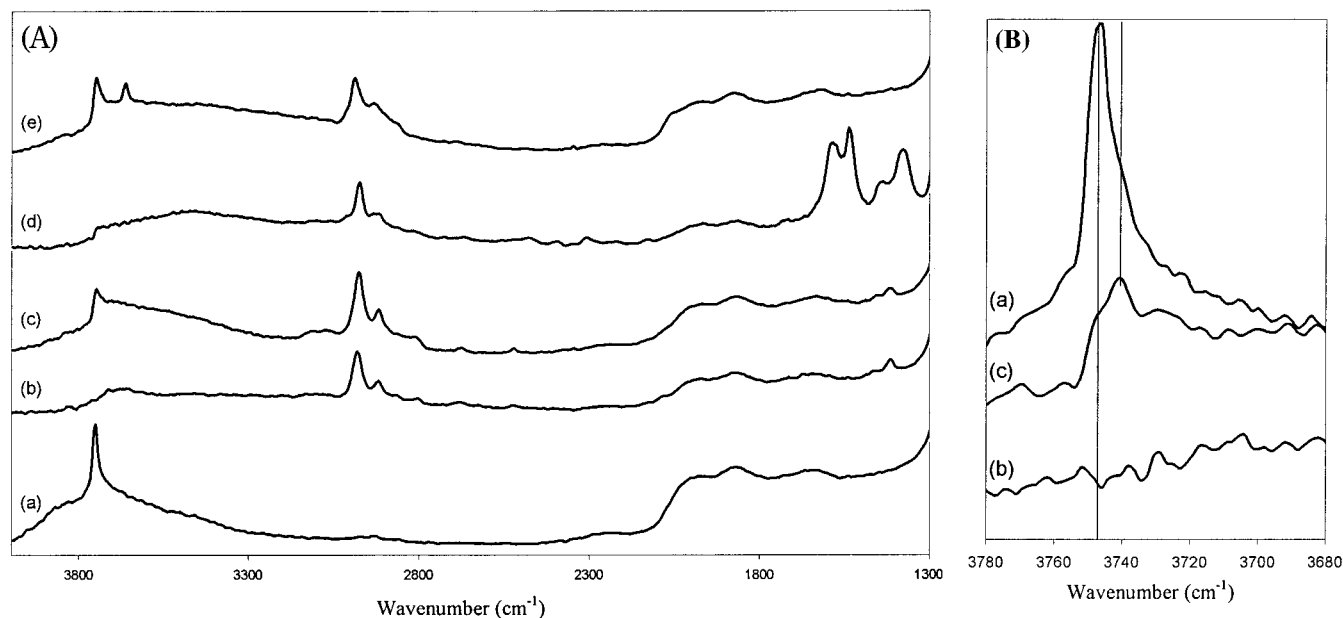


Figure 1. (A) FTIR-PA spectra of (a) blank MCM-48 (b) after reaction with DMDCS, (c) after subsequent hydrolysis, (d) after VO(acac)₂ grafting, and (e) after final calcination. (B) Enlargement of the hydroxyl region of Figure 1A (samples a–c).

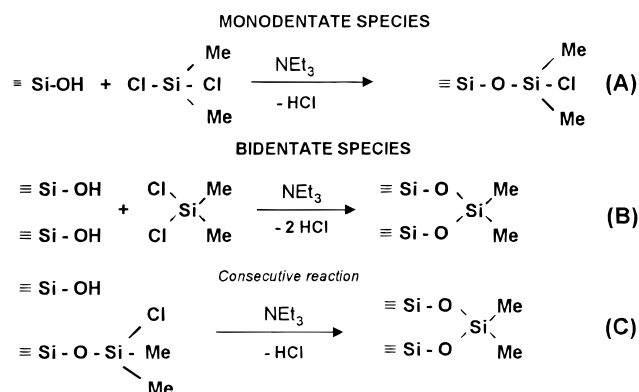
BET method; pore size distribution was calculated using the method of Barret, Joyner, and Halenda.¹³ TGA measurements were recorded on a Mettler TG50 thermobalance.

Raman spectra were taken on a home-built system, composed of Spectra-Physics 2020 series lasers, coupled with a Dilor XY-800 triple spectrometer and a Whight Instruments nitrogen cooled CCD. All samples were measured at room temperature in a backscattering configuration, with 514.53 nm Ar⁺ laser excitation. The laser power was tuned between 1 and 30 mW.

UV–vis diffuse reflectance spectra were taken on a Varian Cary 5 spectrophotometer, equipped with a specially designed Praying Mantis diffuse reflectance attachment of Harrick.

Results and Discussion

Silylation of the MCM-48 Surface. The reaction of (alkyl)-chlorosilanes with a silica surface has been discussed and reviewed in great detail in the literature.¹⁴ Although five different reactions are possible with di-, tri- or tetrachlorosilanes, basically two important surface species are created. The first is a monodentate silyl group, created by the monomolecular reaction of one silanol with one chlorosilane, according to reaction A. The second surface species is a bidentate silyl group, created either by a bimolecular reaction (B) or by a consecutive reaction (C).



We have reported previously¹⁵ that the surface of MCM-48, prepared by the gemini 16–12–16 surfactant, possesses 0.9 OH/

nm². The distribution of the monodentate and the bidentate silyl groups can be calculated as follows.

For reaction A, yielding monodentate groups (MD), one OH that is reacted, yields one Cl on the surface. For the bidentate species (BD), created either by reaction B or C, two OH that are consumed yield no Cl groups. In other words, neglecting the possible formation of other species (MD + BD = 1):

$$\frac{\text{Cl}_{\text{surface}}}{\text{OH}_{\text{reacted}}} = \frac{\text{MD}}{\text{MD} + 2\text{BD}} = \frac{\text{MD}}{2 - \text{MD}} \Rightarrow \text{MD} = \frac{2\text{Cl}_{\text{surface}}}{\text{OH}_{\text{reacted}} + \text{Cl}_{\text{surface}}} \quad (1)$$

In other words, the fraction of monodentate surface species can be easily calculated if the amount of Cl grafted on the surface and the amount of reacted silanols is known.

Parts A and B of Figure 1 show the infrared spectra of the samples before and after silylation. Comparison of infrared spectrum a (blank MCM-48) and infrared spectrum b (silylated MCM material) shows that after a treatment with DMDCS, the free silanol band at 3747 cm^{−1} has completely disappeared and thus that all silanols have reacted. On the basis of chemical analysis (Table 1), it was calculated, using eq 1, that the surface is covered with 20% of bidentate species ((Si–O)₂Si(CH₃)₂), which are completely inert toward further reaction) and 80% of monodentate species (Si–O–Si(CH₃)₂Cl).

Hydrolyzation of the Silylated MCM-48. This sample is hydrolyzed by stirring in liquid water to yield Si–O–Si(CH₃)₂–OH surface groups, which will act as anchors for the vanadium grafting.

A closer inspection of the hydroxyl region (Figure 1B) shows a clear shift in the free hydroxyl band. The original MCM-48 exhibits a free silanol band at 3747 cm^{−1} (spectrum a). Upon reaction with DMDCS, all silanols are consumed (spectrum b). After hydrolysis, a small shoulder at 3747 cm^{−1} is restored, but the main band is positioned around 3738 cm^{−1} (spectrum c). Similar band shifts have been observed for silica, reacted with aminosilanes.¹⁴ This band is consequently assigned to the hydroxyls that are created by the hydrolysis of the Si–Cl groups.

TABLE 1: Chemical and Physicochemical Analysis of the Different Samples

	blank MCM-48	silylated MCM-48	hydrolyzed silylated MCM-48	hydrolyzed silylated MCM-48 after VO(acac) ₂ grafting	hydrolyzed silylated MCM-48 after VO(acac) ₂ grafting and calcination
<i>S</i> (BET)	1396 m ² /g		1147 m ² /g		1080 m ² /g
<i>V_p</i>	1.15 ml/g		0.87 ml/g		0.69 ml/g
<i>a</i> (cubic cell constant)	7.56 nm		7.75 nm		7.69 nm
$\alpha(\text{OH})$	0.9 OH/nm ²				
<i>n</i> (OH)	1.9 mmol/g				
<i>n</i> (Cl)		1.3 mmol/g	0 mmol/g	0 mmol/g	0 mmol/g
<i>n</i> (V)				1.2 mmol/g	1.2 mmol/g
<i>n</i> (acac)				1.2 mmol/g	0 mmol/g

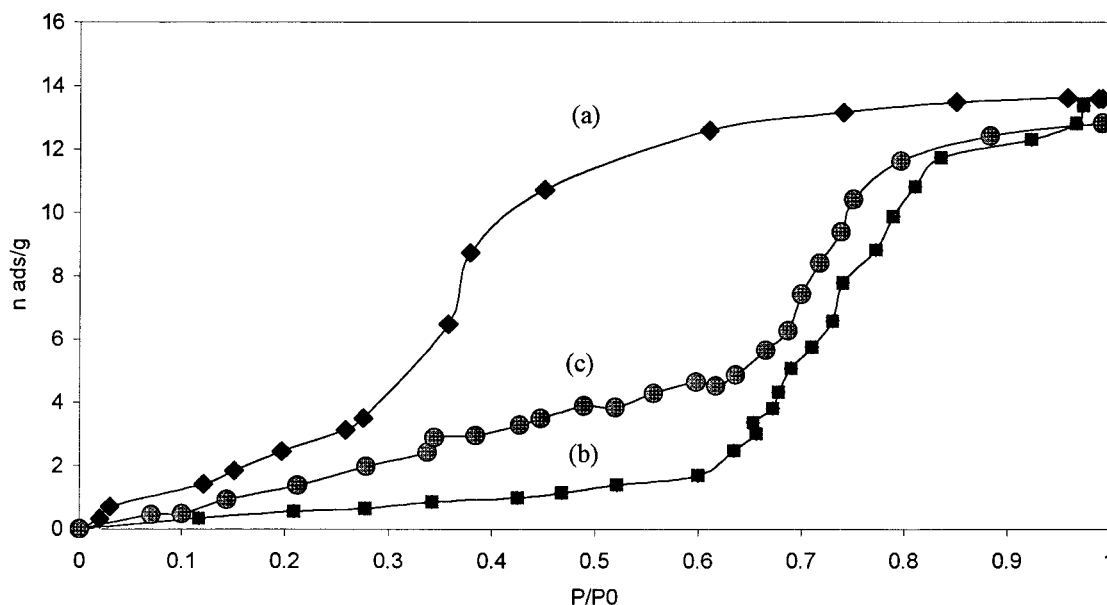


Figure 2. Water adsorption isotherms (25 °C) of (a) blank MCM-48, (b) MCM-48 after reaction with DMDCS and hydrolysis, and (c) sample b after reaction with VO(acac)₂ and subsequent calcination at 400 °C.

A second shoulder can be observed at 3720–3730 cm⁻¹. This band is assigned to the *terminal* silanol of a series of bridged silanols.¹⁴ Although the sample is dried at 300 °C after stirring in liquid water, traces of residual physisorbed water or hydrogen interacting silanols can never be completely avoided. This is also seen in the infrared spectrum of Figure 1A (spectrum c), exhibiting a broad band between 3600 and 3200 cm⁻¹, due to hydrogen interacting species.

EMPA (electron micro probe analysis) confirms that no residual chlorine groups remain on the surface after stirring with water at room temperature for 2 h (Table 1).

Already at this point, the MCM materials are extremely hydrophobic and are no longer miscible with water. This is further evidenced by measuring the water adsorption isotherms of a nontreated MCM-48 (Figure 2a) and the same sample after reaction with DMDCS and subsequent hydrolysis (Figure 2b). Although the total water adsorption remains approximately the same, the condensation of water vapor in the pore of the blank MCM-48 sample already commences at $p/p_0 < 0.4$, whereas in the case of the silylated MCM-48, the vapor condensation is postponed until relative pressures of about 0.7, which clearly shows the strong repulsive behavior of the silylated sample toward water vapor.

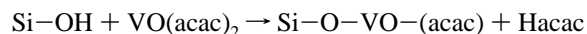
The MCM-48 samples have retained the long-range ordering of the pores and still possess a high surface area and pore volume (see Table 1). X-ray diffractograms and pore size distributions will be discussed in more detail underneath.

Molecular Designed Dispersion of VO(acac)₂ on the Hydrolyzed, Silylated MCM-48. VO(acac)₂ is grafted on the

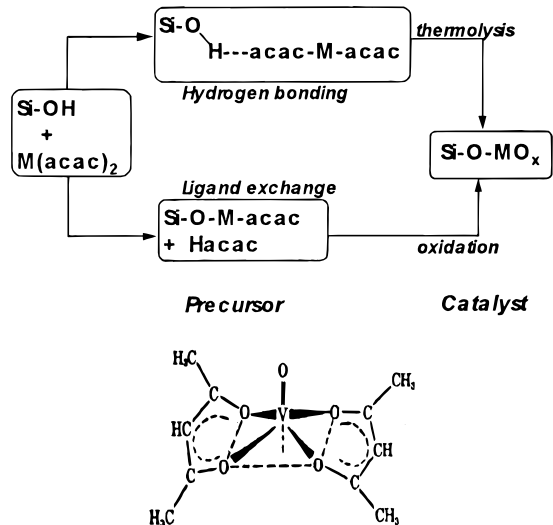
hydrolyzed, silylated MCM-48 surface using the gas-phase molecular designed dispersion method.¹⁵ The use of VO(acac)₂ (vanadylacetylacetonate) to graft VO_x groups on a catalytic support by means of the molecular designed dispersion method has been described in detail in some of our previous publications.^{15–18} In principle, the complex is anchored to the hydroxyl groups of the support by either a hydrogen bonding or by a ligand exchange mechanism. The adsorbed complex is called the precursor. A treatment in air at elevated temperatures converts the adsorbed acetylacetonate complex into metal oxide species that are chemically bonded to the surface. The process and the reagent are visualized in Scheme 1.

The infrared spectrum (Figure 1A,d) shows that all recreated silanols have reacted and that characteristic bands appear in the 1600–1300 cm⁻¹ region, due to the acac ligand.¹⁷

Chemical analysis (Table 1) reveals that the ratio of acac ligands to V centers on the surface is 1 (1.2 mmol/g acac is present on the surface and also 1.2 mmol/g V is grafted on the surface), which means that the reaction has followed a ligand exchange mechanism:



In a final step, this precursor is calcined. The infrared spectrum (Figure 1A,e) clearly shows the V–OH bands appearing at 3660 cm⁻¹,¹⁹ although apparently also a fraction of the silanols has been restored. Furthermore, the presence of the C–H vibrations (around 3000 cm⁻¹) and the absence of the acac vibrations

SCHEME 1: (Bottom) VO(acac)₂; (Top) General Overview of the Molecular Designed Dispersion Process

indicate that the acac ligands have decomposed completely but that the methylsilyl groups are stable toward calcination at 450 °C.

Further information on the structure of the grafted surface species was obtained by Raman spectroscopy. Figure 3 shows the Raman spectrum of the calcined, silylated VO_x-MCM. The shoulder at 1060 cm⁻¹ and the broad band at 800 cm⁻¹ are due to the silica.^{20,21} The strong band at 1040 cm⁻¹ is characteristic for the stretching vibration of terminal V=O bonds in monomeric, tetrahedral vanadia surface species. The presence of crystalline V₂O₅ can be excluded, since even traces of these species produce a very strong band at 996 cm⁻¹. The broad band around 920 cm⁻¹ is assigned to the stretching vibrations of terminal vanadyl groups within a two-dimensional surface phase. The Raman spectrum of Figure 3 therefore suggests that the majority of the surface V species are present as monomeric, tetrahedral species but that a fraction of these species has clustered to form surface polymers. This clustering of a small

fraction of the V-species is consistent with the formation of some silanols in the infrared spectrum.

Overall Reaction Mechanism. Figure 4 presents the overall, idealized reaction mechanism. The surface of MCM-48 contains 0.9 OH/nm², which react completely with DMDCS in the liquid phase, if NEt₃ is used as a catalyst. The majority of the silanols react monofunctionally but a small fraction also reacts further, according to reaction 3 to yield inert, bidentate species. All chlorine functions on the surface are converted toward hydroxyls upon hydrolysis, as no residual Cl groups are detected on the surface after hydrolysis. This hydrolyzed, silylated MCM-48 is visualized in Figure 4 as species A.

The VO(acac)₂ is grafted in a gas-phase reactor onto this silylated, hydrolyzed surface. All recreated silanols react with the VO(acac)₂ in a 1:1 stoichiometry, following a ligand exchange mechanism. This precursor is visualized as species B. Upon calcination at 450 °C, the acac ligands are decomposed but the methylsilyl functions remain intact. Most of the V species are converted into isolated, tetrahedral V^{VO_x} species, as indicated in Figure 4 as species C. Raman spectroscopy provided strong evidence for the presence of a V=O bond in tetrahedral coordination; infrared spectroscopy revealed the presence of V-OH species, EPR spectroscopy (not shown) showed the complete absence of V⁴⁺ species and UV-vis diffuse reflectance showed O to V charge-transfer bands, with V⁵⁺ surrounded by oxygens in a strictly tetrahedral configuration (vide infra). However, a small fraction of the isolated VO_x species clusters to form surface oligomers, as evidenced by the 920 cm⁻¹ Raman band, hereby recreating a fraction of the silanols. This final material (species C in Figure 4) will be referred to further in the text as the "final catalyst".

Figure 5 shows the X-ray Diffractograms of the blank MCM-48 (a) and of the final catalyst. The two diffractograms show a pattern, typical for the cubic MCM-48 structure, with a large diffraction band between 2 and 3 °2θ, assigned to the 211 reflection, a smaller one slightly above 3 °2θ, assigned to the 220 reflection, and a more diffuse band between 4 and 6 °2θ, which is in fact a superposition of the 321, 400, 420, 332, 422, 431, and 521 reflections. There is no significant shift between

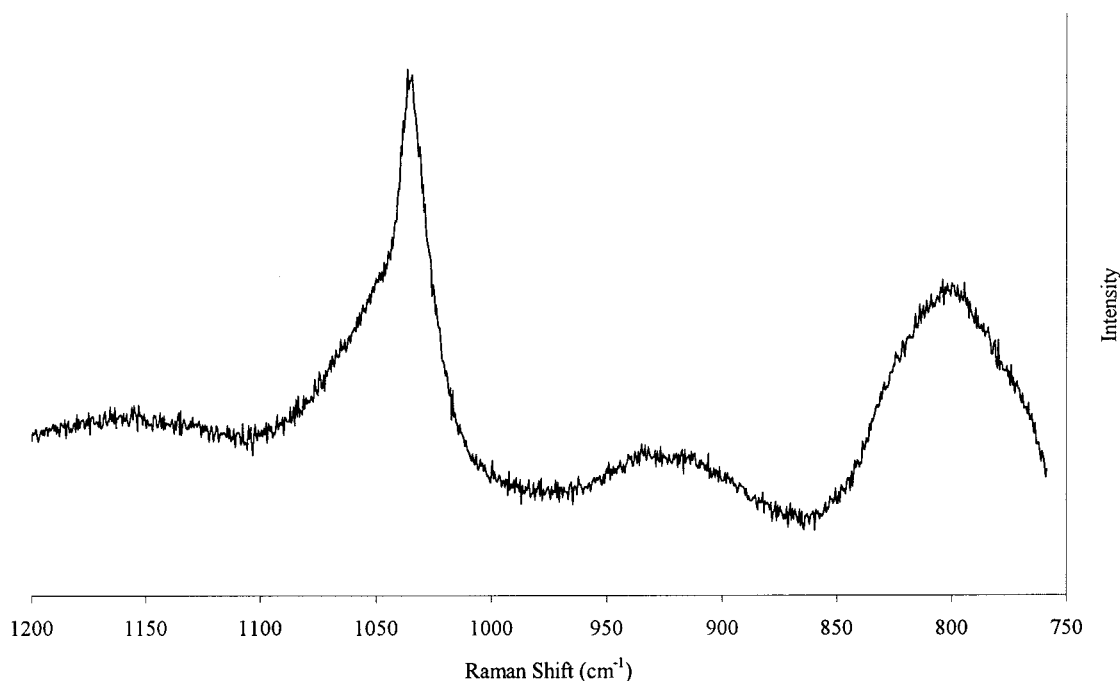


Figure 3. Raman spectrum of the final catalyst.

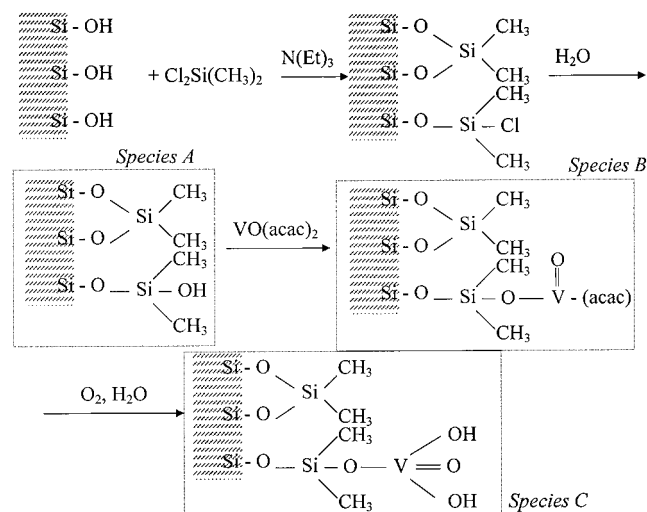


Figure 4. Idealized reaction mechanism.

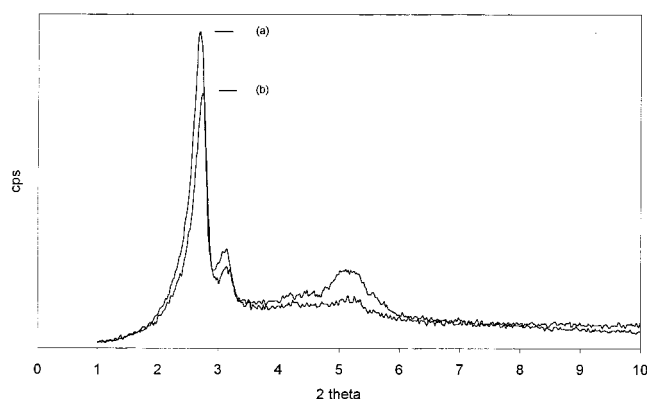
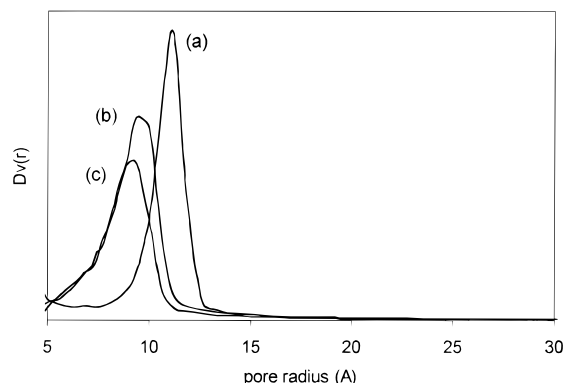


Figure 5. X-Ray diffractograms of (a) original MCM-48 and (b) final catalyst.

Figure 6. Pore size distributions of (a) original MCM-48 (b) after reaction with DMDCS and hydrolysis (species B) and (c) after subsequent reaction with VO(acac)₃ and calcination (species C).

the diffraction bands of both samples, indicating that the unit cell parameter a did not change during the silylation and grafting of VO_x. The values of a are listed in Table 1, being 7.56 nm for the blank MCM and 7.69 nm for the final catalyst. It can be inferred from this figure that the long-range pore ordering of the material has not decreased significantly after these several reaction steps and that the final catalyst still has a high order of crystallinity.

Figure 6 shows that the silylation and subsequent hydrolysis has a pronounced (but expected) effect on the pore size distribution. When the blank MCM-48 (curve a) is silylated, a shift of the pore size distribution is observed toward smaller

TABLE 2: Chemical Analysis of the Stability Towards Leaching

	$n(V)$ on sample (mmol/g)	$n(V)$ leached out (mmol/g)	% V leached out
nonsilylated MCM-48,	1.4	1.2	86
DMDCS-MCM48	1.2	0.2	17
MTCS-MCM-48	1.8	1.2	67

TABLE 3: Chemical Analysis of the MCM Samples, Modified with DMDCS and MTCS, Respectively

	monodentate (%)	bidentate (%)	$n(Cl)$ (mmol/g)	$n(Me)$ (mmol/g)	Me/Cl
DMDCS	80	20	1.3	3.1	2.4
MTCS	60	40	2.1	1.5	0.7

pores (curve b). Upon grafting of VO_x surface species, a second but smaller shift toward smaller pores is observed (curve c). Quantitative data are also presented in Table 1. The final catalyst still has a high porosity with a maximum on the edge of the micro- and mesoporous region. The pore size distribution has not broadened significantly.

Note. At this point, we would like to mention that the conventional BJH method, used throughout this article, probably underestimates the pore maximum of MCM materials by 20–30%. Several independent research groups^{22–24} have reported almost the same values for this underestimation of pores with a radius between 1 and 2 nm. Although some new models have been developed (such as the nonlocal density functional method or the semiempirical method of Zhu et al.²⁴), calculations are laborious and most research groups still use the BJH method, which makes mutual comparison of the data easier. However, the reader should bear in mind that the actual pore size is about 20–30% larger. The BJH method is not used in the calculation of the pore volume or surface area; therefore these values are correct.

Leaching in Liquid Water. A blank, nonsilylated MCM sample, and two silylated MCM samples, using Me₂SiCl₂ (DMDCS) and MeSiCl₃ (MTCS) followed by hydrolysis, were grafted with VO_x using the molecular designed dispersion of VO(acac)₃ as described previously. All three samples were stirred with water for 1 h and the amount of vanadium still present at the surface was determined. The results are presented in Table 2. The nonsilylated blank MCM-48 has lost 86% of the V-loading after this treatment. The MCM-48 that was pretreated with methyltrichlorosilane has lost 67% of the V-loading, and the sample pretreated with dimethyldichlorosilane has only lost 17% of its vanadium loading. Silylation with MTCS obviously results in materials with a much lower Me/Cl ratio on the surface (see Table 3). So, after reaction with MTCS, the surface contains a large amount of hydrolyzable Cl groups and a relatively low amount of hydrophobic methyl groups. Although a large amount of anchoring sites are created by hydrolysis, and therefore a high amount of VO_x species can be grafted onto this surface (see Table 2), the resulting materials are not hydrophobic enough to affect the leaching of the grafted VO_x species in a significant way. Upon silylation with DMDCS, on the other hand, the material is highly hydrophobic (no longer miscible with water) and the stability of the V centers toward leaching is improved enormously.

Water Adsorption. It is important to stress that, despite the high hydrophobicity of the samples, the V⁵⁺ centers are still accessible to water adsorption. This is evidenced by the color change from bright white to dark orange upon standing in ambient air. This color change is caused by water adsorption

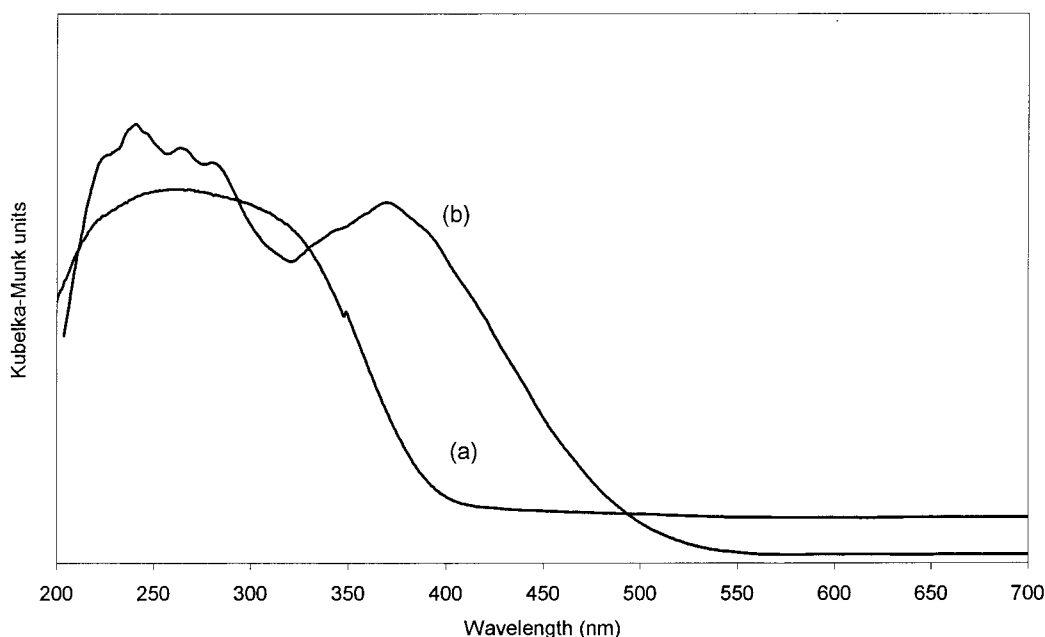
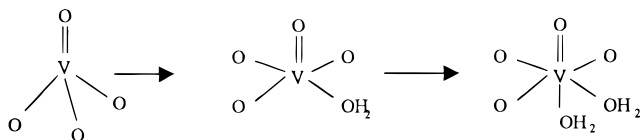


Figure 7. UV-vis diffuse reflectance spectrum of the final catalyst (a) dry and (b) after standing in ambient air for 48 h.

on the V-centers, shifting the position of the L → M charge transfer bands to the visible region, as shown in Figure 7. Several authors have speculated on the mechanisms behind this dramatic color change. The tendency of isolated pseudotetrahedral V^V compounds to increase their coordination sphere by coordinating water molecules has been mentioned in the literature.²⁵ It is now generally agreed that the color change is due to the coordination of ambient water, in which the tetrahedral V^V center coordinates with two water molecules, resulting in a (pseudo) octahedral structure.



The complete accessibility of all V centers is further evidenced by the water adsorption isotherms of Figure 2. Comparison of the water adsorption isotherm b (silylated MCM-48 before VO_x grafting, species B) and adsorption isotherm c (silylated MCM-48 after VO_x grafting, species C) shows that the difference in water uptake at $p/p_0 = 0.6$ (just before water condensation in the pores) is 2.8 mmol/g. If one assumes that one tetrahedral V center adsorbs two water molecules, the concentration of V sites would be $2.8/2 = 1.4$ mmol/g. The experimental value (cfr. Table 1) is 1.2 mmol/g, which is a good indication that all V sites are tetrahedral centers and are accessible to coordinate with two molecules of water.

Hydrothermal Stability. The silylated materials show an unusual structural stability in hydrothermal (high temperature and pressure) conditions. The silylated samples were put in a closed stainless steel vessel on a perforated grid. Underneath the samples, liquid water was introduced and the vessel was tightly closed, after which the entire reactor was heated in a furnace from 100 °C up to 150 °C and kept at this temperature for at least 24 h. The X-ray diffractograms and pore size distributions of the samples after this hydrothermal treatment are presented in parts A and B of Figure 8.

Figure 8A shows that the silylated samples, even after a treatment at 150 °C and 4.7 atm, still show a remarkable

TABLE 4: Effect of Hydrothermal Treatment on the Porosity of Different Samples

	hydrothermal temperature (°C)	hydrothermal pressure (atm)	S(BET) (m ² /g)	pore volume (mL/g)
original MCM-48			1440	1.2
MCM-DMDCS			1077	0.7
MCM-DMDCS	120	2	1025	0.7
MCM-DMDCS	150	4.7	978	0.7
blank MCM-48	120	2	800 ^a	0.5

^a Surface area calculated by the Langmuir method, due to the shift of the pores into the microporous region.

crystallinity, in contrast to a nontreated sample (spectrum d) that has lost completely its crystallinity after a treatment at 120 °C. The same conclusions can be drawn from Figure 8B. The pore size distributions of the silylated samples do not change significantly upon hydrothermal treatments, whereas a blank MCM-48 has lost its mesoporosity after a hydrothermal treatment at 120 °C. Quantitative data on the effect of hydrothermal conditions on different samples are summarized in Table 4, again evidencing that the silylated samples withstand severe hydrothermal conditions without loss in pore volume.

Conclusions

The use of DMDCS as a coupling agent for the grafting of VO_x species on the surface of MCM-48 results in hydrophobic materials, with a high stability toward leaching and structural collapse, but with the V centers still in accessible positions.

The reaction of pure silica MCM-48 with dimethyldichlorosilane and subsequent hydrolysis results in hydrophobic materials with still a high number of anchoring sites for subsequent deposition of vanadium oxide structures. The molecular designed dispersion of VO(acac)₂ on these silylated samples results in a V loading of 1.2 mmol/g. Spectroscopic studies evidence that all V is present as tetrahedral V^V oxide structures, and that the larger fraction of these species is present as isolated species of type C in Figure 4.

These final catalysts are extremely stable in hydrothermal conditions. They can withstand easily hydrothermal treatments at 150 °C and 4.7 atm pressure without significant loss in

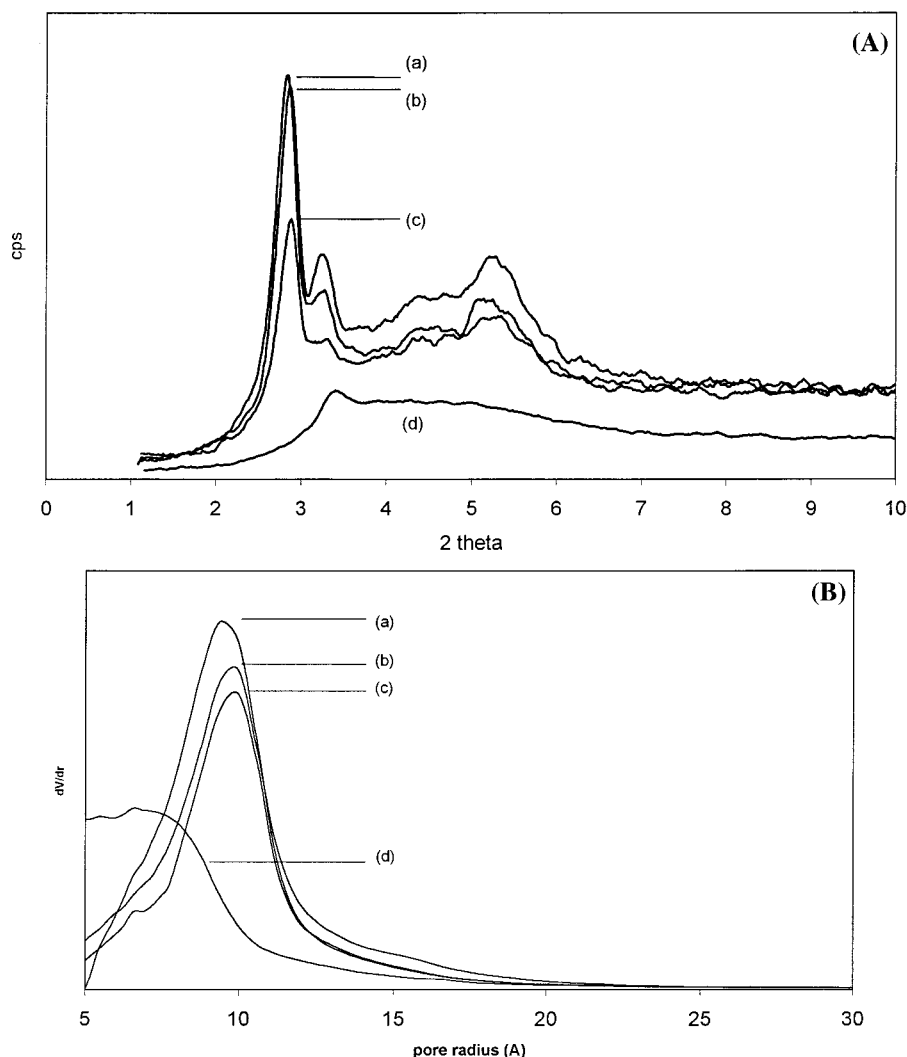


Figure 8. (A) X-ray diffractograms of (a) MCM-48 after reaction with DMDCS and hydrolysis (species B), (b) after hydrothermal treatment at 120 °C (2 atm), and (c) after hydrothermal treatment at 150 °C (4.7 atm). (d) blank MCM-48 after hydrothermal treatment at 120 °C. (B) Pore size distributions of the same samples.

crystallinity or porosity. Also, the leaching of the V in aqueous conditions is reduced with at least a factor 4.

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