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Stabilized MCM-48/VO$_x$ catalysts: synthesis, characterization and catalytic activity

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Abstract

The high synthesis cost, the poor hydrothermal stability of the pore structure and the extensive leaching of the active metal sites in liquid phase heterogeneous catalysis are three of the most important drawbacks for the industrial use of the newly developed mesoporous crystalline materials (MCM-41, MCM-48, HMS, FSM, ...). In this study, we present an integrated approach that tackles these three problems simultaneously. High quality MCM-48 is prepared by a method of surfactant extraction and recuperation. The surface of the material is stabilized using a bifunctional silane, rendering the surface essentially hydrophobic, but leaving sufficient secondary anchoring sites for a further activation with VO(acac)$_2$ and final calcination. The final catalyst is thoroughly characterized and its catalytic and mechanical behavior is evaluated. It is shown that these materials can withstand severe hydrothermal conditions and that the leaching of the catalytic active species in liquid media is very strongly reduced. The obtained catalysts are active and selective and can be regenerated without significant loss of activity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: MCM-48; Hydrophobization; Stabilization; Hydrothermal stability; Vanadium catalyst

1. Introduction

In spite of the numerous recent advances in the synthesis and catalytic activation of mesoporous silicate materials (M41S, including MCM-41 and MCM-48; HMS; SBA; MSU), still some important drawbacks remain, limiting the industrial use of these materials in catalytic applications [1].

The rather difficult and long synthesis procedure, the lack of data on the possibilities of upscaling, and — even more importantly — the high cost of the reagents renders these materials far too expensive for bulk industrial use. The possible applications of these support materials are therefore mainly situated in the production of fine chemicals and pharmaceutical products, as the added value of the end products is very high for these processes and the quantity of required catalyst is relatively low. The development of catalysts for these processes is a newly born, exciting discipline, as until now, non-catalyzed stoichiometric processes have been widely used in the synthesis of fine chemicals and pharmaceuticals [2].

Secondly, most mesoporous silicate materials are known to be insufficiently stable, especially in hydrothermal steaming conditions or in aqueous media [3]. The thermal stability of these supports is sufficient, as most materials can resist temperatures up to 700°C before collapsing. The mechanical stability has been investigated recently, and is more than sufficient to withstand typical treatments such as pressing and molding [4].

The main problem is therefore the water attack on the siloxane bridges of the walls. Since the wall of an

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MCM-48 is typically about 1 nm thick, corresponding to only a few $[SiO_4]^{4-}$ groups, the structure collapses in even mild hydrothermal conditions.

A third problem, typical for heterogeneous liquid phase reactions, is the leaching out of the active (transition) metal in aqueous media. This limitation is not typical for the mesoporous supports, as the problem is known for decades for zeolitic and amorphous catalysts. Some scattered remedies for these problems have been proposed in literature, but the solutions that are presented usually focus on one isolated aspect of the problem.

Extracting and reusing the surfactant can largely reduce the cost of the synthesis of the mesoporous supports. The stability of the materials in aqueous or hydrothermal conditions has been improved by reacting the surface with a trimethylsilylating agent, such as hexamethyldisilazane or trimethylchorosilane [5–7]. Although this treatment might be very effective in se, it creates a completely hydrophobic and inert material, with no residual anchoring sites to graft an active catalytic component.

We will present an integrated approach that deals with the three cited problems simultaneously. An MCM-48 support is prepared by a controlled extraction of the cationic gemini surfactant, in such a way that no thermal post-treatment step is required. Secondly, we perform a partial hydrophobization of the silica walls, using dimethyldichlorosilane (DMDCS), rendering it essentially hydrophobic to withstand the water attack, but creating simultaneously sufficient active sites for a subsequent grafting of the surface. Finally, VO_x surface species are grafted on the silylated MCM-48 surface, in such a way that leaching is almost completely suppressed.

2. Experimental

Pure silica MCM-48 was prepared using the gemini 16-12-16 surfactant (general formula $[C_nH_{2n+1}N^+(CH_3)_2\text{–}(CH_2)_s\text{–}N^+(CH_3)_2C_mH_{2m+1}] \cdot 2Br)$, as described previously [8]. In this case, the surfactant was not burnt-out, but extracted by a 9:1 vol.% MeOH/conc. HBr mixture. The material was silylated using appropriate amounts of $Cl_2Si(CH_3)_2$ (DMDCS) and $N(C_2H_5)_3$, 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. $VO(acac)_2$ was anchored on the silylated surface using the gas phase molecular designed dispersion method [9–12]. Finally, the sample was calcined at 450°C.

Infrared spectra were measured on a Nicolet 5DBX spectrometer, equipped with an MTEC photo-acoustic detector. X-ray diffractograms were recorded on a Philips PW1840 powder diffractometer, using Ni-filtered Cu Kα 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 BET method. The mesoporous pore size distributions are calculated by the recently developed KSJ (Kruk–Sayari–Jaroniec) model [13]. TGA measurements were recorded on a Mettler TG50 thermobalance.

The gas phase oxidation of methanol was carried out in a fixed-bed continuous flow reactor at 400°C and atmospheric pressure. Prior to the reaction 0.2 mg catalyst was treated by flowing a He/O_2 mixture at 400°C for several hours. An 80 ml/min $He/O_2/MeOH$ (88/8/4 mol.%) flow was used as reactant mixture. Reaction products were analyzed by gas chromatography on a $2\,m \times \frac{1}{8}$ in. Porapak T column (Alltech). The catalytic activity and selectivity were measured at the steady state, which was reached after 1 h time-on-stream.

The liquid phase selective oxidation of toluene was carried out at 80°C using 40 ml acetonitrile as a solvent, 4.8 ml toluene, 0.4 g catalyst and 1 ml of TBHP (tert-butyl-hydro-peroxide). At fixed time intervals, liquid was pipetted out, filtered and injected in a GC, equipped with a 30 m × 0.25 mm Alltech AT-1 column at 160°C. Prior to the injection, residual oxidant was decomposed with MnO_2.

3. Results and discussion

3.1. The synthesis of MCM-48 using gemini surfactants and controlled surfactant extraction

MCM-48 is one of the mesoporous crystalline supports that exhibit a cubic symmetry. It has a very

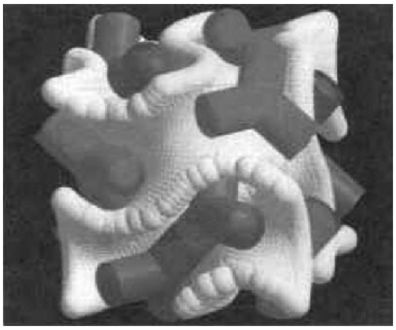

Fig. 1. The MCM-48 Ia3d cubic structure. Rods represent surfactant.

narrow and tunable mesoporous pore size distribution, surface areas exceeding 1200 m^2/g and pore volumes higher than 1 ml/g. The cubic structure of the MCM-48 material is drawn in Fig. 1. In the early years, MCM-48 was somewhat neglected with respect to its MCM-41 counterpart, due to its difficult and irreproducible synthesis. Fortunately, the use of the so-called gemini surfactants and the introduction of a hydrothermal condensation step have greatly improved the quality of these materials and facilitated their synthesis [8].

The structure directing surfactant is usually removed by a simple temperature programed calcination, thus burning out the surfactant which comprised up to 60 wt.% of the precursor. Surfactant extractions are an elegant, economically and ecologically attractive alternative and have been attempted previously, but mainly for HMS materials (mesoporous silicas, prepared using *neutral* amines as the surfactant). Due to the much weaker S^0I^0 interaction, compared to the S^+I^- interaction, these surfactants can be extracted easily by a simple polar solvent, such as ethanol [14–16]. Some reports have been published on the extraction of cationic surfactants (typically the cetyltrimethylammonium salt), but the resulting material is mostly inferior to the calcined one and in all cases, still a post-treatment at high temperatures is required to remove the residual organics [17–19].

We have optimized an extraction procedure for MCM-48 that does not require a post-treatment and that produces materials with a better quality than the calcined ones [20].

TGA measurements showed that 90–95 wt.% of the surfactant is extracted by this procedure. Elemental analysis, X-ray diffraction and infrared analysis proved that the recrystallized extracted surfactant is identical to the original one and we have re-used it several times without any decrease in the quality of the obtained MCM materials.

The extracted and the calcined materials show clearly different characteristics. This is exemplified by the pore size distributions, as calculated by the recently published KSJ method [5–7]. Although in most studies, the conventional BJH method is used to calculate the mesoporous pore size distributions [21], it is now generally accepted that this method produces large errors, especially for supra-micropores and small mesopores, with pore dimensions in the region 2–6 nm. The error increases from zero for pore diameters above 8 nm to almost 40% for pore diameters of 2 nm. At the moment, a lot of work is being performed to update the non-local density functional theory for mesoporous silica materials [22], since it was originally calibrated using active carbon as a reference material and applicable DFT models may be expected soon.

However, we have chosen to use the semi-empirical KSJ model of Kruk–Sayari–Jaroniec [13], which is easily applicable due to its simplicity and validity in a broad pore region. It is also one of the few models that allows to differentiate between hydrophilic and hydrophobic surfaces. Although originally developed for honeycomb structures, extensive testing on high quality MCM-48 has satisfied us that the model can also be used for the cubic mesoporous structures [23,24].

Fig. 2A and B shows the isotherms and the KSJ pore size distributions of extracted and calcined materials, respectively. Isotherm c in Fig. 2A is one of a ‘fourth cycle’ MCM-48, meaning that the surfactant is extracted and re-used for the fourth time. After these four cycles, the amounts of material became too small to allow a subsequent extraction and the material in this case is simply calcined. The isotherm still strongly resembles the isotherm of a calcined MCM-48, prepared with fresh surfactant. The surface area of the MCM-48 prepared with the fresh solvent is 1450 m^2/g, of the one with the recovered surfactant is 1350 m^2/g. Pore volumes are 1.3 and 1.1 ml/g, respectively.

Fig. 2B evidences that the MCM-48, prepared by surfactant extraction, has a larger pore size and a narrower pore size distribution, compared to the calcined samples. It can be speculated that the oxidative decomposition of the surfactant at high temperatures

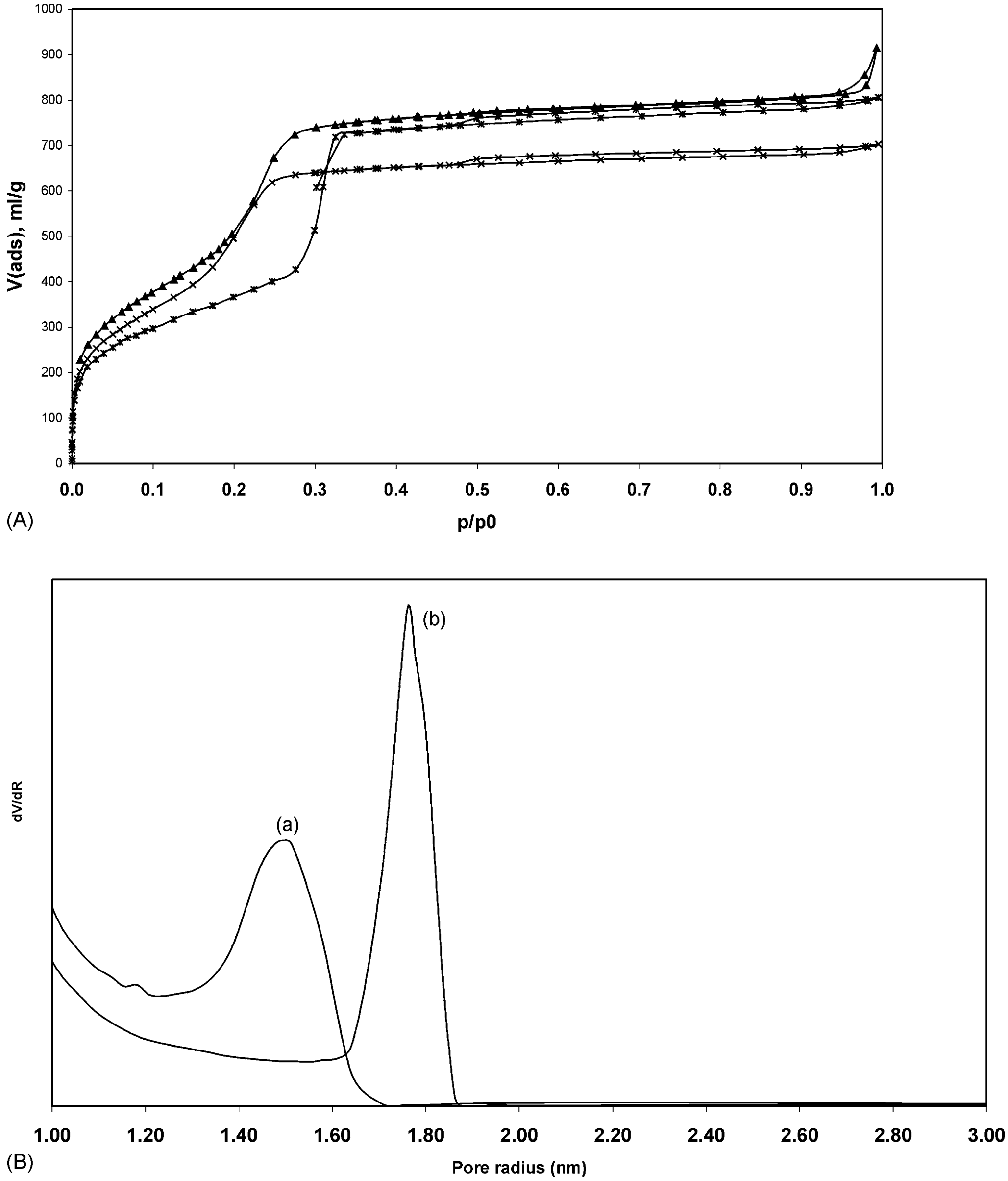

Fig. 2. (A) Nitrogen adsorption isotherms of a calcined MCM-48 (▲), an extracted MCM-48 ($*$), a calcined MCM-48, prepared by re-used surfactant (×); (B) KSJ pore size distributions of a calcined MCM-48 (a), an extracted one (b).

causes very high local temperatures, resulting in a slight structural collapse and thus a slightly broader pore size distribution. XRD analysis confirms these observations; the cubic unit cell for the calcined MCM-48 is calculated to a amount 8.04 nm, whereas the unit cell for the extracted MCM-48 is 8.54 nm.

3.2. Synthesis of hydrophobic and catalytic active MCM-48/DMDCS/VO$_x$ catalysts

The general strategy to obtain stable, hydrophobic and catalytic active materials is presented in Fig. 3.

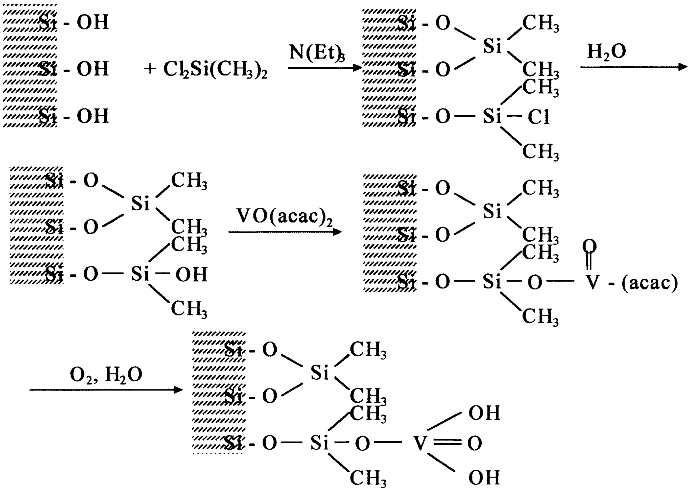

Fig. 3. General reaction scheme for the synthesis of stable and active MCM-48 supported VO_x catalysts.

In the first step, the isolated silanols of an MCM-48 support are reacted in the liquid phase with dimethyldichlorosilane, using triethylamine as a catalyst. This reaction has been extensively discussed in literature [25]. Chemical analysis established that the surface is covered with 20% of bidentate species ($(Si–O)_2Si(CH_3)_2$, which are completely inert towards further reaction) and 80% of monodentate species ($Si–O–Si(CH_3)_2Cl$).

This sample is hydrolyzed by stirring in liquid water to yield $Si–O–Si(CH_3)_2OH$ surface groups, which will act as anchors for the vanadium grafting.

The different reaction steps can be easily followed by the photo-acoustic infrared spectra in Fig. 4 and by the chemical analysis data in Table 1. Upon reaction with the DMDCS, all free silanols at 3747 cm^{-1} of the untreated MCM-48 support (spectrum a) disappear and typical methyl vibrations appear (spectrum b). After stirring in liquid water for 1 h and subsequent drying, a new silanol band appears (spectrum c), due to the hydrolysis of the Cl groups. Chemical analysis showed that no residual Cl groups remain on the surface (Table 1).

In a subsequent step, $VO(acac)_2$ is grafted on the hydrolyzed, silylated MCM-48 surface using the gas phase molecular designed dispersion method. 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 infrared spectrum (spectrum 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. Chemical analysis reveals that the ratio of acac ligands to V centers on the surface is 1, which means that the reaction has followed a ligand exchange mechanism:

$$Si–OH + VO(acac)_2 \rightarrow Si–O–VO–(acac) + Hacac$$

In the final step, this precursor is calcined at 450°C. The infrared spectrum (spectrum e) clearly shows the V–OH bands appearing at 3660 cm^{-1} [26], 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 indicate that the acac ligands have decomposed completely, but that the methylsilyl groups are stable towards calcination at 450°C.

3.3. Structural and catalytic evaluation of the final catalysts

3.3.1. Mechanical stability

The mechanical stability of an MCM-48 and a silylated MCM-48 was compared by pressing the powders

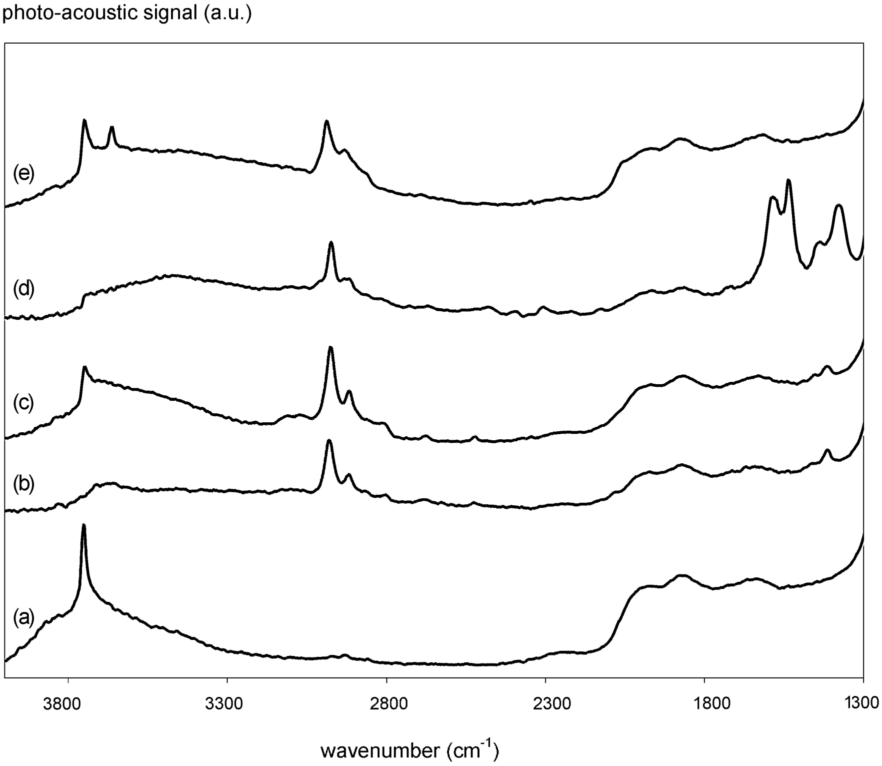

Fig. 4. FTIR-photo-acoustic spectra of: (a) blank MCM-48; (b) after reaction with DMDCS; (c) after subsequent hydrolysis; (d) after grafting of VO(acac)$_2$; (e) after final calcination in air.

Table 1
Chemical and surface analysis of the MCM-48 during the different steps of stabilization and activation

	Blank MCM-48	MCM-48/DMDCS (before hydrolysis)	MCM-48/DMDCS (after hydrolysis)	MCM-48/ DMDCS/VO(acac)$_2$	MCM-48/ DMDCS/VO$_x$	MCM-48/Vo$_x$
S (BET) (m^2/g)	1396		1147		1080	1120
V_p (ml/g)	1.15		0.87		0.69	0.74
a (cubic cell constant) (nm)	7.56		7.75		7.69	7.65
α(OH)	0.9 OH/nm^2					
n(OH) (mmol/g)	1.9					
n(Cl) (mmol/g)		1.3	0	0	0	0
n(V) (mmol/g)				1.2	1.2	1.4
n(acac)				1.2	0	0

in a conventional 13 mm dye, using pressures from 1 to 10 tons[1] under ambient conditions. A good resistance towards unilateral pressure and compaction is important for the industrial processing of the catalysts, by pressing and grounding them into uniform sized particles.

The XRD patters of the pressed and grounded samples are presented in Fig. 5, whereas an untreated MCM-48, grafted with VO$_x$ species, loses its structural integrity after a mild pressing at 3–4 tons, the

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[1] 1 ton for a 13 mm dye corresponds to 740 bar.

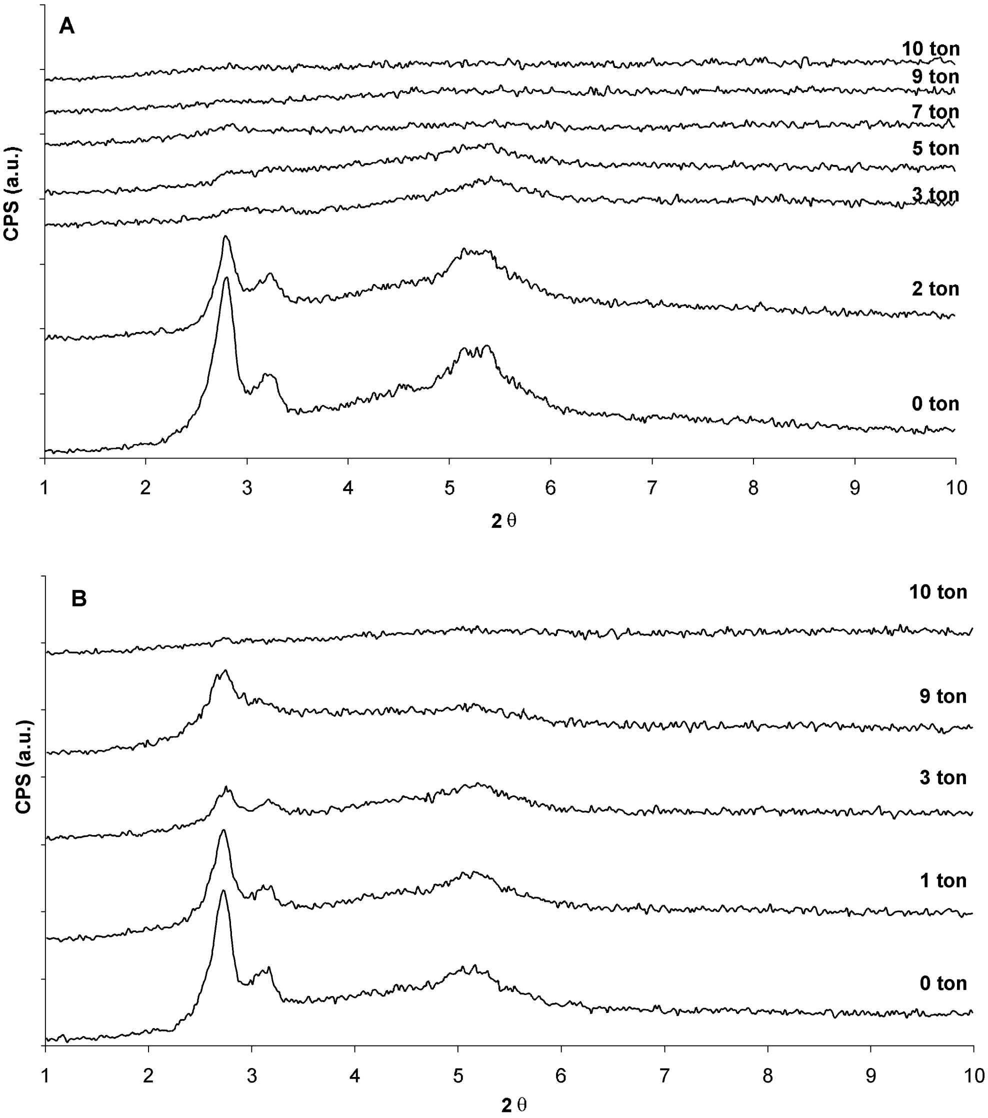

Fig. 5. X-ray diffractograms of (A) MCM–VO$_x$ (non-silylated); (B) MCM–DMDCS–VO$_x$ (silylated) as a function of mechanical pressure. Unilateral pressure, in a conventional 13 mm dye, expressed in tons. Pressures were kept constant for 10 min.

MCM-48, pretreated with DMDCS, can easily resist pressures up to 8–9 tons, without significant loss of crystallinity or porosity.

It was already mentioned several times that the structural decay of MCM-48 is mainly caused by water attack on the highly strained siloxane bridges. It is also suggested that moisture in the atmosphere under which the solid is compressed is responsible for the siloxane hydrolysis and that a compression under nitrogen is less critical [27,28]. The hydrophobic surface of the silylated sample is able to resist these high pressures much better than the untreated samples, although the actual wall thickness of the samples has changed only very slightly (1.0 nm for the untreated MCM-48; 1.2 nm for the silylated sample, as determined by the method of Schumacher et al. [29].

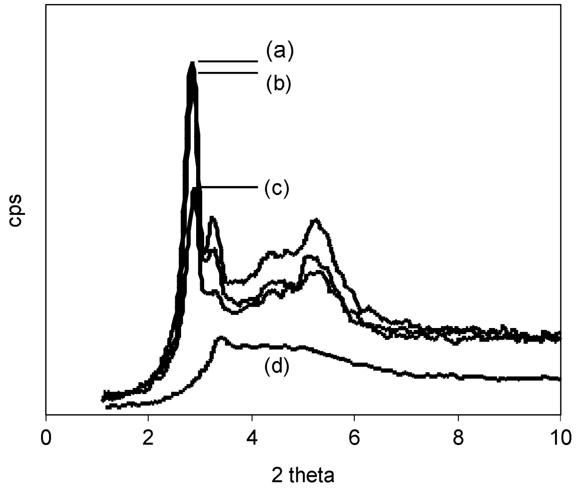

Fig. 6. XRD patterns of: (a) silylated MCM-48; (b) after hydrothermal treatment at 120°C and 1.95 atm; (c) 160°C and 6.1 atm; (d) non-silylated MCM at 120°C and 1.95 atm.

3.3.2. 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 up to 150°C and kept at this temperature for at least 24 h. The X-ray diffractograms of the samples after this hydrothermal treatment are presented in Fig. 6, evidencing that the silylated samples, even after a treatment at 150°C and 4.7 atm, still show a remarkable crystallinity, in contrast to a non-treated sample (curve d) that has lost completely its crystallinity after a treatment at 120°C.

3.3.3. Catalytic activity and selectivity

The catalytic behavior of the DMDCS treated materials is compared to samples on which the active functions are directly grafted to the surface. Both the catalytic activity (in gas and liquid phase) and the leaching behavior of the active sites are compared. The concentration of active sites on the surface and the physical characteristics such as surface area and pore volume are very similar for both catalysts (see Table 1, two final columns), justifying this comparison.

The gas-phase oxidation of methanol is an important probe reaction to study the catalytic properties of surface vanadium oxide species [30,31]. The product selectivity reflects the reaction pathway that depends on the concentration of acidic, basic or redox sites on the catalyst surface. Acidic sites give rise to dimethyl ether, basic sites produce carbon oxides (CO_x) and redox sites produce formaldehyde, methyl formate and dimethoxymethane. Silica supported vanadium oxides show a rather low activity for the oxidation of methanol in comparison to other frequently used oxide supports like alumina and titania. However, VO_x/SiO_2 catalysts are very selective towards formaldehyde.

Table 2 shows the conversion and selectivity of both tested samples. It can be inferred from this table that the conversion of methanol of the silylated catalyst is even higher than that for the non-silylated catalyst. However, the formaldehyde selectivity is lower, in favor of the formation of dimethylether. This is a confirmation for the hypothesis that the surface of the silylated catalysts is slightly more acidic, which is most probably caused by the presence of the slightly acidic V–OH surface species. Indeed, we have shown in previous papers [32] that the adsorption and subsequent calcination of $VO(acac)_2$ on bare silica surfaces (either amorphous silica or MCM-48)

Table 2
Conversion and selectivity of the gas phase selective methanol oxidation

	MCM-48/VO_x catalyst			MCM-48/DMDCS/VO_x catalyst		
	300°C	350°C	400°C	300°C	350°C	400°C
Conversion (%)	24	38	55	48	80	84
Selectivity of formaldehyde (%)	60	85	85	21	44	58
Selectivity of dimethylether (%)	15	8	5	67	52	30
Selectivity of methylformate (%)	20	5	2	2	0	0

Table 3
Conversion and selectivity of the liquid phase selective oxidation of toluene

	MCM-48/VO$_x$ catalyst	MCM-48/DMDCS/VO$_x$ catalyst
Toluene conversion (1 h) (%)	5	5
Toluene conversion (24 h) (%)	11	12
Selectivity of benzaldehyde (%)	100	100

results in the formation of VO$_x$ tetrahedral surface oligomers, which posses very few V–OH groups but numerous V–O–V linkages. In contrast, as we have shown above, the pre-grafting of DMDCS produces surfaces that are mainly characterized by isolated, tetrahedral, monomeric Si–O–V(O)(OH)$_2$ species. This difference in surface structure is clearly visible by a different catalytic behavior.

In the context of possible applications for selective oxidations of larger (pharmaceutical) products, the selective oxidation of toluene with TBHP is an excellent probe reaction to study the stability and leaching of the catalyst. The results of the liquid phase selective oxidation of toluene are summarized in Table 3. There are no fundamental differences in catalytic behavior between the two catalysts. Both catalysts are 100% selective towards benzaldehyde. Turn-over frequencies can be calculated to amount about two conversions per site per hour, which is very comparable to catalytic systems, described in literature [33,34].

Inspection of Fig. 7 on the other hand shows dramatic difference in the leaching behavior of these catalysts. The non-silylated MCM-48/VO$_x$ catalyst loses almost 85% of its V-sites upon stirring in liquid water for 1 h at room temperature and more than 50% of its V-sites after a catalytic run in acetonitrile at 80°C for 24 h. This makes this material obvious not suitable of heterogeneous liquid phase catalysis, as the observed reaction is probably heterogeneous and the catalyst is non-recyclable.

The MCM-48/DMDCS/VO$_x$ catalyst, however, loses less than 15% of its V-sites by stirring in liquid water, and even less that 10% of its sites during the 24 h catalytic run. Both leaching in liquid water and in acetonitrile is therefore reduced by a factor of 5 by the DMDCS treatment.

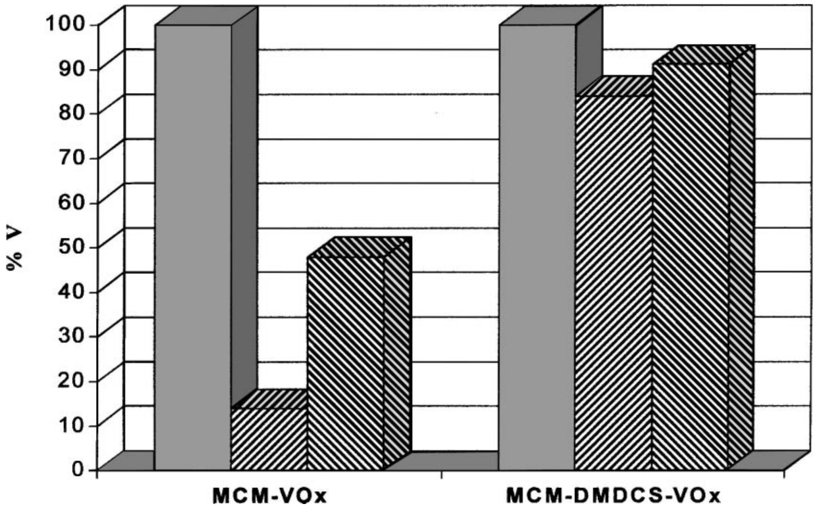

Fig. 7. Leaching of the V-species for a non-silylated (MCM–VO$_x$) and silylated (MCM–DMDCS–VO$_x$) sample expressed in percentage V remaining after 1 h stirring in liquid water (///) and after 24 h refluxing in the catalytic mixture with acetonitrile as a solvent (\\\\).

Moreover, the catalyst is easily regenerated by a calcination in air at 400–450°C. Studies to further reduce the leaching of the active sites virtually to 0 are currently being performed.

4. 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 towards leaching and structural collapse, but with the V-centers still in accessible positions. These V-species are almost exclusively present on the surface as isolated, tetrahedral $Si–O–V(O)(OH)_2$ species and do not form surface polymers.

These final catalysts are extremely stable towards unilateral pressing and in hydrothermal conditions. They can withstand easily hydrothermal treatments at 160°C and 6.1 atm pressure without significant loss in crystallinity or porosity. Also, the leaching of the V-centers is very strongly reduced.

The pretreatment with DMDCS does not affect the catalytic activity, nor the selectivity of the catalysts. On the contrary, the catalytic activity is slightly increased for the silylated samples, probably due to the increased hydrophobicity of the catalytic surface.

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