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Great Improvement of Chromatographic Performance Using MCM-41 Spheres as Stationary Phase in HPLC

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Grafted MCM-41 materials are ordered mesoporous adsorbents suitable for reversed-phase liquid chromatography applications (RP-HPLC): they possess high surface area, which is a great advantage to enhance the thermodynamic behavior of the classical stationary phase by increasing solute retention. Hence, MCM-41s allow the separation of poorly retained solutes which are hard to separate on conventional silica gels. Furthermore, the ordered porosity in MCM-41 enhances the kinetic properties of the classical stationary phase. MCM-41s afford higher and more homogeneous molecular diffusivity, which increases the column efficiency for high flow rates as compared to that of classical silica-based columns. Besides, RP-HPLC provides a meaningful description of the particle size distribution at a macroscopic scale and of the pore ordering by probing the diffusivity of solutes. MCM-41s obtained by pseudomorphic synthesis of silica gel have successfully passed all the chromatographic tests and the results show that this new synthesis pathway really allows independent control of the pore size and the particle size of MCM-41. Spherical particles of 5 μm of MCM-41 without aggregation have been synthesized by this route and are revealed as very good candidates for stationary phases in RP-HPLC.

Introduction

The MCM-41 type ordered mesoporous adsorbents disclosed by Mobil[1] in 1992 have attracted much attention in the past decade. The self-assembly of surfactants aggregates and mineral species can now be tailored to provide mesoporous materials with high surface areas, extremely narrow pore size distribution, and perfectly adjustable pore size. MCM-41 silicas have then been proposed as possible stationary phases for size-exlusion chromatography,[2] normal-phase HPLC,[3,4] capillary-gas chromatography,[5] and chiral HPLC.[6,7] However, to bring a substantial improvement to the existing stationary phases, those MCM-41 phases should first exhibit chromatographic efficiency comparable to the later. As particle-size scattering seriously affects the plate height and consequently the separation process, the development of those materials in chromatography requires a perfect control of size and shape of the particles. HPLC columns are usually packed with spherical particles. The particle diameter usually ranges from 3 to 7 μm; the lower the particle diameter is, the less important the peak broadening is and the better the column efficiency is. The preparation of spheres of micelle-templated silicas (MTS) as MCM-41, HMS, or MSU with predetermined monodispersed size of particles has been the target of several research groups in the past few years. The Stöber conditions[8] have been applied to the synthesis of MCM-41 spheres,[9] but the resulting particles are small or aggregated and exhibit poor efficiency in chromatography. A good particle growth control can be obtained around the isoelectric point of silica (pH 2). Various studies reported the synthesis of 5-μm MSU-X spheres within this pH range.[10−13] However, the result-

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ing particles are not isolated and form aggregates that cannot always be distinguished by scanning electron microscopy. As a result, the chromatographic separation exhibits plate height much higher than expected for monodisperse spheres of 5 μm. Other processes, much heavier technologically, such as spray-drying[14,15] or oil-drop,[16] have been proposed to form spheres. However, no evidence has been found that it would allow the synthesis of monodisperse spheres in the 5-μm range. Pseudomorphic synthesis of MCM-41 is a new way of synthesis recently reported[17] and represents an easy way to overcome those difficulties. This kind of synthesis uses preformed silica particles with the adequate size and shape. This work addresses the synthesis of 5-μm-MCM-41 stationary phase and the chromatography results obtained with it in reversed phase HPLC (RP-HPLC). Some great improvements of an ordered porous structure (MCM-41) compared to a disordered one (silica gel) as commercial stationary phase will be shown.

Experimental Section

Materials. MCM-41 samples were synthesized according to the pseudomorphic synthesis procedure described previously.[17] Preformed silica spheres were used: Nucleosil 100-5 and Nucleosil 120-5 purchased from Macherey Nagel (5-μm spheres) and LiChrospher 100 provided by Merck (15-μm spheres). The resulting MCM-41 will be noted as Nu100-MCM-41, Nu120-MCM-41 and LiC-MCM-41, respectively. The reactions were performed in a steel autoclave with the proportions 1:0.25:0.1:20 $SiO_2/NaOH/CTAB/H_2O$. Reactants were added under stirring, and the mixture was mechanically stirred (400 rpm) for half an hour at room temperature and put at 388 K for 20 h. The resulting solids were recovered by filtration, washed with water, and dried at 353 K overnight. Materials were then calcined under air flow at 823 K for 8 h.

Functionalized Materials. Silica surfaces were further functionalized with octyl chains according to a commonly used procedure[18] that was previously shown to give one of the best surface coverages of silica.[19] Chlorodimethyloctyl silane was added to a stirred suspension of outgassed MCM-41 (453 K for 12 h) in anhydrous refluxing toluene, then 5 molecules of grafting agents and 5 molecules of pyridine per nm^2 of the parent material were added. The reagents were then stirred for 15 h under reflux at 393 K under nitrogen flow. The powders were filtered and washed successively with toluene, acetone, acetone/water, acetone, chloroform, and ether. The samples were dried under vacuum at 393 K overnight.

Characterization. Materials were characterized by powder X-ray diffraction (XRD) for MCM-41 type materials (Cu Kα radiation, CGR Theta 60 diffractometer with Inel Drive), N_2 sorption isotherm at 77 K (Micromeritics ASAP 2000), and scanning electron microscopy (SEM) (Hitachi). The grafted chain loadings were calculated from the carbon and silicium contents given by elemental analysis.[19]

Chromatographic Tests. The chromatographic columns (50 mm × 4 mm) were prepared with the different materials by the slurry method. The grafted materials were dispersed in carbon tetrachloride−dioxane and packed in the column under 550 bar with methanol. Around 0.5 g of stationary phase was contained in the columns.

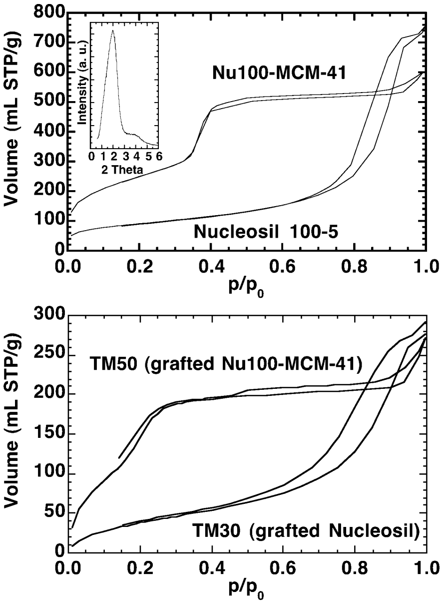

Figure 1. Nitrogen sorption isotherms at 77 K of (top) Nucleosil 100-5 and Nu100-MCM-41 obtained by pseudomorphic synthesis of the former, and (bottom) TM30 and TM50 octyldimethyl-grafted Nucleosil 120-5 and Nu100-MCM-41. Inset: XRD pattern of Nu100-MCM-41.

Table 1. Textural Features of Crude Silica Materials: Nucleosils, LiChrospher, and MCM-41s

material	V_p (mL/g)	S_{BET} (m^2/g)	D_{pore} (Å)	d_p-SEM (μm)
Nucleosil 120−5	0.53	198	145	5
Nu120-MCM-41	0.61	916	37	5
Nucleosil 100-5	1.11	329	160	5
Nu100-MCM-41	0.79	913	39	5
LiChrospher 100	1.27	396	146	15−20
LiC-MCM-41	0.72	911	38	15−20

The HPLC system consisted of two Shimadzu LC10AD pumps (France), a Rheodyne model 7125 injection valve (5-μL sample loop), and a Shimadzu SPD6A spectrophotometer detector set at 254 nm with an 8-μL cell.

Alkylbenzenes were purchased from Sigma Aldrich (France). Water was distilled and deionized. Acetonitrile and methanol were HPLC grade from SDS (France).

Two conventional silica-based stationary phases have been compared to the MCM-41 materials: a ZorbaxSBD-C8 (5 μm, 150 mm × 4.6 mm), an octyl-grafted silica gel, and a Kromasil-C18 (5 μm, 150 mm × 4.6 mm), an octadecyl-grafted silica gel.

For all the experiments, the columns were thermostated at 303 K using a water bath.

Results and Discussion

Materials. XRD and nitrogen sorption isotherms at 77 K (Figure 1) results show that the pseudomorphic synthesis of LiChrospher and Nucleosils into MCM-41s have given expected results for well-ordered MCM-41 (Table 1). Cell parameters are around 50 Å, surface areas are as high as 900 m^2/g, pore volumes are around 0.70 mL/g, and pore sizes are around 40 Å. MCM-41 materials have lower pore volume and smaller pore size than silica gels, but differ essentially from silica gels by their higher surface area (900 instead of 400 m^2/g) and their ordered and uniform porosity. This is evi-

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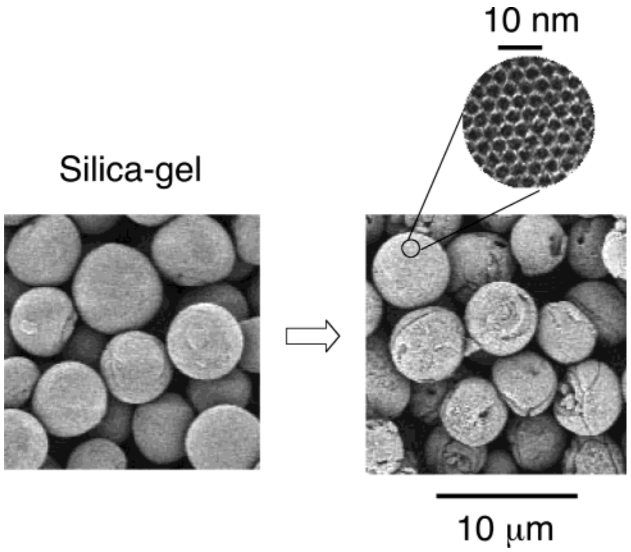

Figure 2. SEM pictures of Nucleosil 100-5 silica gel and its transformation by pseudomorphic synthesis into MCM-41 (Nu100-MCM-41).

denced in Figure 1 for Nu100-MCM-41 by the sharp step in the nitrogen adsorption isotherm correponding to a pore diameter of 39 ± 1 Å and the two order peaks in the XRD pattern, whereas the pore diameter of the corresponding parent silica (Nucleosil-100) is 150 ± 40 Å without any order revealed by XRD. MCM-41s are silica materials without interconnections between pore channels of the same size. SEM pictures show the conservation of shape and size of the initial silica particles used in the synthesis (Figure 2). No aggregation between spherical particles is observed by SEM in the pictures of MCM-41 obtained by pseudomorphic synthesis, which is one of the biggest challenges in the synthesis of ordered silica mesostructures.

The silica materials, Nucleosils and LiChrospher, as well as the MCM-41s obtained from these silica sources, were grafted with chlorodimethyloctylsilane in the presence of pyridine. Nitrogen adsorption isotherms of grafted materials show that the pore diameters, the pore volumes, and the surface areas decrease for all materials after grafting. The pore size of MCM-41 is around 25 Å, and is exactly 27 ± 2 Å for the grafted Nu100-MCM-41 (TM50) in Figure 1, whereas silica gels provide pore size around 120 Å and 120 ± 50 Å for grafted Nucleosil 100 (TM30) in Figure 1. The decrease in pore size of 12 Å in MCM-41 shows that the octyl chains are bent on the surface at 77 K (temperature of nitrogen isotherm) and an average decrease of pore size of 30 Å for silica will be consistent with the length of two straight octyl chains. Grafted MCM-41 keeps an ordered porosity, as evidenced by the pore size distribution of ±2 Å, whereas silica gels exhibit a larger pore size distribution after grafting (±50 Å), evidenced by a hysteresis loop extending on a large pressure domain. Although MCM-41 materials present smaller pores, they retain a significant surface area (~600 m^2/g). The amount of grafted chains/nm^2 of initial material is slightly lower on MCM-41 materials (1.1−1.6 octyl chains/nm^2 representing 1.8−2.6 $\mu mol/m^2$) compared to that on silicas (1.7−1.8 octyl chains/nm^2 representing 2.8−3 $\mu mol/m^2$) (Table 2). The lower initial silanols density in MCM-41 materials (2 $SiOH/nm^2$) compared to that in silicas (5 $SiOH/nm^2$) can explain this difference. SEM pictures show the preservation of shape and size of the silica particles after the grafting procedure. Chromatographic tests have been performed on all grafted materials displayed in Table 2.

Table 2. Features of the Octyldimethylsilane-Grafted Silica Materials Used as Stationary Phase in Reverse-Phase Chromatography

material	parent material	V_p (mL/g)	S_{BET} (m^2/g)	D_{pore} (Å)	octyl chains/nm^2	d_p-SEM (μm)
TM30	Nucleosil 120-5	0.41	159	129	1.70	5
TM31	Nu120-MCM-41	0.26	605	26	1.04	5
TM50	Nu100-MCM-41	0.28	564	27	1.16	5
TM20	LiChrospher 100	0.86	269	141	1.79	15−20
TM15	LiC-MCM-41	0.26	550	24	1.61	15−20

Chromatographic Tests on the Grafted Materials. The different grafted materials have been tested by inspecting chromatographic peaks obtained under various conditions. We were interested in both (a) solute retention to study the thermodynamic behavior of the materials (solute interaction with the stationary phase) and (b) peak width to study their kinetic properties (solute dispersion into the column), to see if materials such as MCM-41, due to their ordered porosity, may provide improvement in chromatography. A chromatographic peak is characterized by its retention time, t_r, followed in the first study (a), and by its width, ω, followed in the second study (b).

(a) Study of Solute Retention on the Octyl-Grafted MCM-41s. The retention time depends on the column dead volume, V_m, the mobile phase flow-rate, F, and the retention factor, k, according to

$$t_r = \frac{V_m}{F}(1 + k) \tag{1}$$

The dead volume is given by

$$V_m = \frac{\pi d_c^2 L}{4}\epsilon \tag{2}$$

with d_c being the internal column diameter, L, the column length, and ϵ, the total porosity determined by eluting a nonretained solute.

The definition of the retention factor is given by the following equation:

$$k = K\frac{V_s}{V_m} \tag{3}$$

where K is the distribution constant of the solute between stationary and mobile phases, and V_s/V_m is the phase ratio. K depends on the stationary and mobile phases, the solute, and temperature.

The ability for a chromatographic system to separate a given pair of solutes 1 and 2, may be expressed by the selectivity coefficient, α:

$$\alpha = \frac{k_2}{k_1} = \frac{K_2}{K_1} \tag{4}$$

where k_1 and k_2 are the retention factors and K_1 and K_2 are the distribution constants for solutes 1 and 2.

Theoretically, for a given mobile and stationary phase (octyl chains for example) and assuming that the dead

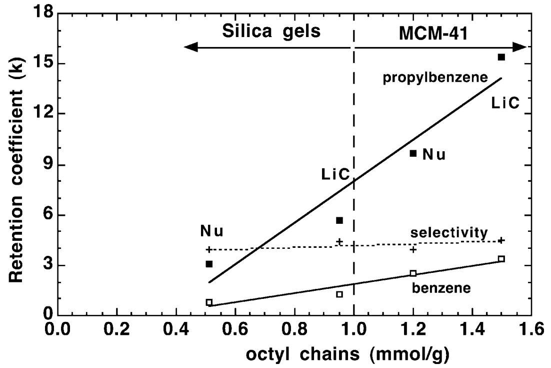

Figure 3. Retention factors of benzene and propylbenzene and selectivity of the corresponding pair versus the amount of grafted octylchains per g of stationary phase for the different grafted materials TM20, TM30, TM31, TM15 (see Table 2) obtained from Nucleosil 120-5 (Nu) and LiChrospher 100 (LiC).

volume is independent of the tested material, k only varies with V_s, the volume or the amount of octyl chains present in the column. In the same conditions, the selectivity coefficient α will theoretically be independent of the tested material as it depends only on K_1 and K_2.

For the octyl-grafted materials TM30, TM20, TM15, and TM31 obtained from Nucleosil 120-5, LiChrospher 100, LiC-MCM-41, and Nu120-MCM-41, respectively, the retention factors and the selectivity have been calculated for the elution of benzene and propyl benzene with a water−methanol (70/30 v/v) mobile phase. All the chromatographic columns have been filled with around 0.5 g of stationary phase. The number of moles of octyl chains/g of stationary phase has been calculated from the grafting density, expressed in chains per nm^2 (Table 2), and silica surface areas of the parent materials (Table 1). The results are plotted in Figure 3.

As expected, the selectivity coefficient of propylbenzene and benzene ($\alpha = 4$) does not vary with the number of chains per g of stationary phase. That proves that the retention mechanism (hydrophobic) is independent of the parent material.

Furthermore, as theoretically expected, there is a good linear correlation between k and the number of chains per g (or per column) of stationary phase. The MCM-41s exhibit higher retention factors than silica gels despite a lower octyl chain density (chains number/nm^2) (see Table 2). In fact, the low grafting density for the MCM-41s is largely compensated by their high surface areas (m^2/g).

Compared to silica gels, these high retentions with MCM-41s may be very advantageous in case of poorly retained solutes that are hard to separate on silica gels.

(b) Study of Solute Dispersion on the Octyl-Grafted MCM-41s. The chromatographic peak is usually assumed to be Gaussian, and the peak width at half-height, ω, is then related to the standard deviation, σ, by $\omega = 2.35\sigma$.

The column efficiency is expressed by the plate number, N, which is determined by

$$N = \frac{t_r^{\,2}}{\sigma_t^{\,2}} \tag{5}$$

with σ_t being the standard deviation expressed in time units.

The plate height, H, is related to both column length, L, and N by

$$H = \frac{L}{N} \tag{6}$$

For a given solute, H varies with the linear velocity, u, related to the flow-rate by

$$u = \frac{LF}{V_m} \tag{7}$$

The variation of H as a function of u may be expressed by the Knox equation.[20] By using reduced parameters h and ν defined by

$$h = \frac{H}{d_p} \tag{8}$$

$$\nu = \frac{u \cdot d_p}{D_m} \tag{9}$$

with d_p being the mean particle size diameter and D_m the molecular diffusion coefficient of the solute in the mobile phase, the Knox equation is given by

$$h = A\nu^{1/3} + \frac{B}{\nu} + C\nu \tag{10}$$

The A term depends on both the quality of the column packing and the contribution of slow mass transfer across the moving stream, the B term accounts for longitudinal diffusion, and the C term expresses the effect of mass transfer resistances in both stagnant and stationary phases. In case of low ν values, the second contribution (B/ν) of the Knox equation is predominant, whereas the third term ($C \cdot \nu$) becomes predominant in case of high ν values. It is well-known that the minimum h value, h_{opt}, is close to 2−3 for good column packings. For estimating the particle size, a relationship, $H = f(u)$, was derived from eq 10 as follows

$$H = A'u^{1/3} + \frac{B'}{u} + C'u \tag{11}$$

The resulting curve presents a minimum ($H_{opt} = h_{opt} \cdot d_p$) which corresponds to the optimum u value (u_{opt}) as shown in Figure 4 for TM15, the grafted LiC-MCM-41 material, for the dispersion study of propylbenzene. For TM15, $H_{opt} = 45$ μm (Table 3) will correspond to apparent particles size $15 < d_p < 22$ μm, in perfect agreement with the particle sizes of the initial LiChrospher 100.

$H = f(u)$ curves have been determined for the different grafted materials with propylbenzene as solute and with a mobile phase H$_2$O/MeOH (30:70). The plate height, H, was calculated after measuring the peak standard deviation (eqs 5 and 6) for various values of u from 0.01 to 0.5 cm/s. For both octyl-grafted silica gels, TM30 and TM20 obtained from Nucleosil 120-5 and LiChrospher 100, respectively, as well as for TM15, obtained from LiC-MCM-41, the $H = f(u)$ curves present a minimum. The corresponding optimum values are listed in Table 3. The particle diameters have been estimated from eq

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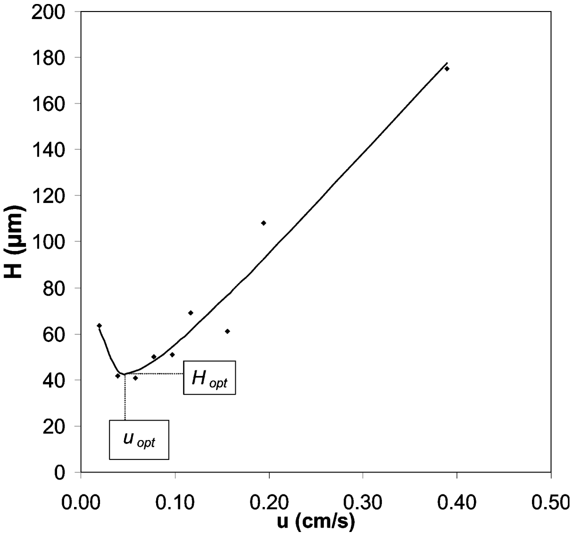

Figure 4. Experimental height plate *H* values versus linear velocity, *u*, fitted with eq 11 for the LiC-MCM-41 stationary phase: solute, propylbenzene; mobile phase, H_2O/MeOH (30:70).

Table 3. Optimum Values of Plate Height and Linear Velocity for the Octyldimethylsilane-Grafted Silica Materials, Calculated by Fitting Experimental Values to $H = f(u)$ Equation (Eq 11). Apparent Particle Diameter Values Estimated from Eq 8 with $h_{opt} = 2-3$, Compared to SEM Particle Size (Solute, Propylbenzene; Mobile Phase, H_2O/MeOH (30/70))

material	parent material	H_{opt} (μm)	u_{opt} (cm/s)	apparent d_p (μm)	d_p-SEM (μm)
TM30	Nucleosil 120−5	12	0.10	4−6	5
TM31	Nu120-MCM-41	125	0.01	42−62	5
TM50	Nu100-MCM-41	12	0.10	4−6	5
TM20	LiChrospher 100	38	0.05	13−19	15−20
TM15	LiC−MCM-41	45	0.04	15−23	15−20

8 and reported in Table 3. These values are in very good agreement with those observed by SEM (Tables 1 and 3) and measured by laser granulometry.[17] This excellent correlation proves, on the one hand, that particles are correctly dispersed and nonaggregated and, on the other hand, that the column packing process has been efficient enough.

Surprisingly, for TM31 (the grafted Nu120-MCM-41 synthesized according to the pseudomorphic synthesis procedure described in the Experimental Section) the plate height remains very high even for the optimum *u* value. Furthermore, the estimated particle diameter (Table 3) is 10 times larger than the particle diameter observed on SEM pictures, which means that an agglomeration of the silica particles probably occurs during the pseudomorphic synthesis, which was not evidenced by SEM analysis.

To overcome this aggregation problem, another synthesis of MCM-41, called Nu100-MCM-41 has been performed from another source of silica, Nucleosil 100-5, exhibiting larger pore volume, with a different procedure using a more diluted synthesis mixture (50 H_2O/Si instead of 20 H_2O/Si) and a shorter synthesis time. From SEM pictures, it was verified that Nu100-MCM-41 conserved the spherical shape and the size of 5 μm of the initial silica Nucleosil 100-5. Nu100-MCM-41 was then grafted with octyl chains (TM50), and tested in propylbenzene dispersion. The peak widths were measured for different flow rates and the $H = f(u)$ curves were plotted. With this optimized synthesis procedure, the MCM-41 issued from Nucleosil (TM50) is characterized by a $H = f(u)$ curve presenting a minimum, for which corresponding optimum values of plate number and linear velocity, reported in Table 3, are in good agreement with particle diameters of 5 μm. This result proves that no aggregation has occurred. During the pseudomorphic synthesis, special care should be taken when the precursor silica gel is formed of very small particles: it requires specific synthetic conditions to avoid particle aggregation, particularly a more dilute solution. It is noteworthy that the particle size determination can be given by the chromatographic test of solute dispersion. Indeed, the chromatographic test represents a definite macroscopic characterization of the particle size of the material performed on 0.5 g samples, whereas SEM analysis is performed on an aliquot of sample. On that account, TM31 does not show aggregation on SEM pictures relative to the fraction of the sample observed under the microscope, while the chromatographic test of solute dispersion was exhibiting particle size 10 times higher.

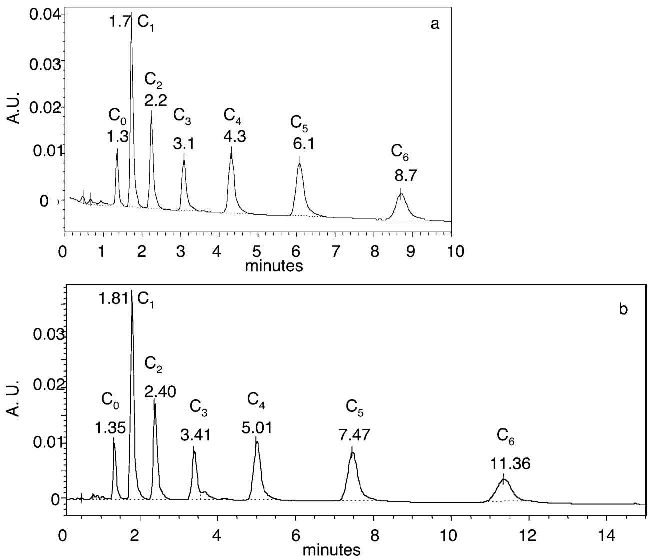

Figure 5. Separation of 7 alkylbenzenes (C_0, benzene to C_6, hexylbenzene) on TM50 (grafted Nu100-MCM-41) with H_2O/ACN (40:60 v/v) (a) and H_2O/MeOH (30:70 v/v) (b): flow rate, 1 mL/min (0.2 cm/s); temperature, 303 K; 5 μL injected.

The TM50, grafted Nu100-MCM-41 appeared to be the best of the MCM-41s in terms of efficiency, with performances comparable to those of traditional grafted silica gels. Hence, this stationary phase has been selected for further studies and for comparison with two commercial stationary phases: ZorbaxSBD-C8 and Kromasil-C18.

Further studies on TM50, Grafted Nu100-MCM-41. The dead volume has been determined by measuring the retention volume of the polystyrene (0.39 mL). The corresponding porosity, $\epsilon = 0.62$ (eq 2), was equivalent to that of the commercial stationary phase ZorbaxSBD-C8 ($\epsilon = 0.60$).

Figure 5 shows the separation of alkylbenzenes obtained with a water−acetonitrile (40:60 v/v) mobile phase (chromatogram (a)) and with a water−methanol (30:70 v/v) mobile phase (chromatogram (b)). These solute retentions have been compared to those obtained under the same conditions with an octyl-grafted silica

Table 4. Experimental Conditions and *C* Values for the Knox Curves Shown in Figure 7 for TM50, the Octyl-Grafted Nu100-MCM-41 (MCM-41 obtained from Nucleosil 100-5 by Suitable Pseudomorphic Synthesis Route)

stationary phase	mobile phase	*t* (K)	solute	$D_m^{(a)}$ ($\times 10^{-5}$cm^2/s)	retention factor	*C*
TM50	water−MeOH (30:70)	298	benzene	0.76	2.6	0.1
TM50	water−MeOH (30:70)	298	toluene	0.73	4.1	0.087
TM50	water−MeOH (30:70)	298	propylbenzene	0.68	9.6	0.07
Kromasil-C18	water−ACN (20:80)	293	butylbenzene	1.5	3.5	0.47

[a] From refs 22 and 23.

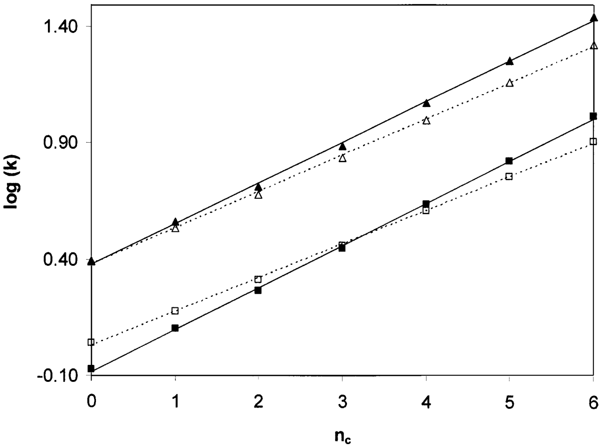

Figure 6. log(k) (retention factors) versus n_c (number of carbons in the alkyl chain of the alkylbenzenes) on TM50 (grafted Nu100-MCM-41) in water−methanol 30:70 v/v (▲), in water−acetonitrile 40:60 v/v (△), and on ZorbaxSBD-C8 in water−methanol (■) 30:70 v/v, in water−acetonitrile 40:60 v/v (□) at 303 K for alkylbenzenes (n_c from 0 to 6).

gel, ZorbaxSBD-C8. As both TM50, grafted Nu100-MCM41, and ZorbaxSBD-C8 are grafted with octyl chains, it is interesting to compare their solute retention. The variation of log *k* with the alkyl chain length (or the number of carbon atoms (n_c) of the alkyl chain in Figure 6) of the eluted alkylbenzenes is reported on Figure 6 for both stationary phases and both mobile phases. In all cases, a linear relationship between log *k* and n_c is observed. This linearity is frequent in the case of RP-HPLC of a homologous series such as alkylbenzenes. Furthermore, the selectivity coefficient for each pair of successive homologues (i.e., the slope of the linear curve) is exactly the same for both phases when using the same mobile phase and suggests that the retention mechanism is homoenergetic for both stationary phases.[21] However, it is noteworthy that the retentions are much higher on TM50 than on ZorbaxSBD-C8 as previously observed for other silica gels. This aspect can be considered for TM50 as an advantage for the separation of the less hydrophobic solutes that are poorly retained on conventional bonded silica gels even when the mobile phase is pure water.

The Knox curves have been plotted for three alkylbenzenes (benzene, toluene, and propylbenzene) with TM50 and compared to the one obtained for the butylbenzene with a Kromasil-C18 stationary phase (Figure 7). The solute D_m values were taken from the experimental study of Li and Carr[22] and adapted to our experimental conditions using the Wilke and Chang equation.[23] Table 4 lists the experimental conditions for the four curves and the obtained results. The *C* term of the Knox equation (eq 10) is dependent on the retention factor. In the case of TM50, this term decreases when the retention factor increases. It has been shown that this phenomenon mainly occurs when the molecular diffusivity into the stationary phase is high, which means that the mass transfer resistance is low.[24] This last result is confirmed by the comparison of the values of *C* for the TM50 and the Kromasil-C18 (Table 4). For a suitable comparison, the *C* values must correspond to the same retention coefficient values, *k*. Hence, it is possible to compare the benzene or the toluene for TM50 to the butylbenzene for the Kromasil-C18. The results listed in Table 4 show that the *C* term is about 5 times lower for TM50. This result confirms that the resistance of mass transfer is very low with the MCM-41 stationary phases as it is with monolithic columns. This last point shows the great improvement obtained with TM50 compared to traditional commercial stationary phases. This low increase in *h* while increasing *ν* is indeed a great improvement. It will allow faster solute analysis without losing column efficiency. This unusual behavior of more homogeneous molecular diffusion into the porous structure is probably due to the very high regularity of the linear porous system in MCM-41 compared to the disordered and tortuous pore network in silica gels. If pore interconnectivity is claimed as necessary with classical porous materials, the lower degree of pore interconnectivity and the pore order lead to improved efficiency properties of MCM-41.

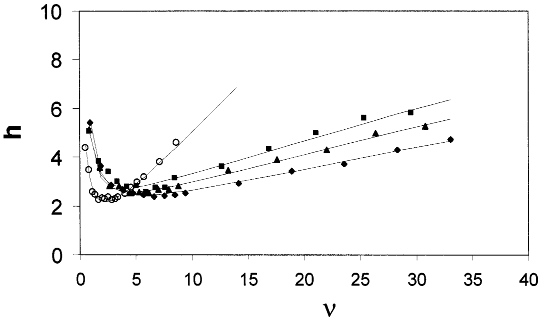

Figure 7. *h* versus *ν* fitted with the Knox equation (eq 10) for TM50 (grafted Nu100-MCM-41) with benzene (■), toluene (▲), and propylbenzene (◆) as solutes and for Kromasil-C18 with butylbenzene as solute (○). See Table 4 for details.

Conclusion

The new way of synthesis of MCM-41 spheres by using preformed silica particles, called pseudomorphic synthesis, offers the possibility to well control the synthesis at both the nanometer and the micrometer

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scales and allows avoidance of the agglomeration of the silica particles. The hierarchical and independent control of porosity and morphology in MCM-41 enabled to serious improvement of the chromatographic performance compared to classical commercial columns. The unique texture of MCM-41 presents two main advantages. The very high surface area leads to much higher retentions. And, above all, the ordered porosity enhances the column efficiency for high flow rates compared to classical silica-based columns, by providing higher and more homogeneous molecular diffusivity. This offers the possibility to separate compounds much faster without a significant loss in column efficiency. HPLC has also revealed the advantage of an ordered porosity of an adsorbent in separation processes which brings MCM-41 particles close to monolithic stationary phases in terms of diffusivity. For all these reasons, MCM-41s are very good candidates for stationary phases in RP-HPLC.

In addition, a chromatographic methodology, like the solute dispersion test, that relies on a narrow distribution of spherical particles, appears to be a meaningful tool to characterize the actual particle size distribution of materials; SEM analysis does not provide such macroscopic information and can be easily misleading.

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