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Tailoring the Hydrophobic Character of Mesoporous Silica by Silylation for VOC Removal

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MCM-41 and non-ordered mesoporous silica were modified using hexamethyl-disilazane (HMDS). The hydrophobic and hydrophilic properties of grafted materials were studied and compared to a purely all silica BEA zeolite by using competitive and noncompetitive water toluene adsorption. A linear correlation between the silylation degree and the hydrophobicity measurements has been found for MCM-41 materials. Even if highly silylated MCM-41 material have more hydrophilic sites (silanol groups) than all silica zeolite, water molecule condensation is not observed because these sites are isolated. Thus, the highly silylated MCM-41 sample exhibits not only hydrophobicity 2.3 times higher than all silica BEA zeolite but also possesses a storage capacity for toluene and chlorobenzene 3 times higher than this zeolite. In competition with water, the organic molecule (toluene or chlorobenzene) adsorption is always favored even if water adsorption is enhanced by chlorobenzene polarity.

Keywords adsorption; hydrophobicity; MCM-41; mesoporous silica; silylation

INTRODUCTION

Activated carbons and hydrophobic zeolites with high Si/Al ratio are usually employed in the removal of Volatile Organic Compounds (VOCs) in wastewater or gas streams. These solids are microporous adsorbents with a limited pore aperture leading to a low diffusion of heavy molecules. Even if these adsorbents are able to adsorb VOCs for low relative pressures, their porous volumes offer a lower sorption capacity than supermicroporous or mesoporous adsorbents and their narrow pores could be blocked more easily leading to difficult desorption steps. A large BET surface and a relevant pore volume confer to MCM-41 materials high sorption capacities. The MCM-41 pore system consists of a hexagonal packing of cylindrical channels having diameter between 1.5 and 10 nm (1). Furthermore, the channel aperture can be tailored with a narrow size distribution by using the appropriate chain length for the templating surfactant (1), by swelling the surfactant assembly through an expender organic molecule (1,2) or by post-synthesis modifications such as thermal restructuring (3), or silylation of hydroxyl groups (4–11). These solids have been reported by several studies to be hydrophobic (12–16) and able to adsorb, in spite of their mesoporosity, relevant quantities of organics compounds such as benzene (16–20), n-hexane (16,17,21), carbon tetrachloride (17), toluene (12,18,22–25), lindane (26), and alcohols (12,18,22). Nevertheless, there are few studies dealing with the adsorption of organics in competition with water for these solids (12,15).

To take advantage of the large sorption capacity of mesoporous solids, it is important to control their hydrophobicity degree and their pore size distribution. The aim of the present work is to establish a correlation between the hydrophobicity and the silylation degree of the MCM-41 samples in order to obtain by silylation very hydrophobic materials. Quantitative hydrophobicity measurements have been obtain from the results of competitive water-toluene adsorption experiments under dynamic conditions (27,28). In a second part, the toluene and chlorobenzene sorption behavior on mesoporous materials with the highest hydrophobicity have been compared with a purely all silica hydrophobic BEA zeolite in absence and presence of water.

EXPERIMENTAL

Materials

MCM-41 is a purely all silica mesoporous material synthesised according to procedures developed by MOBIL researchers using cetyltrimethylammonium bromide (CTMAB) as a structure directing agent (29). The CTMAB surfactant was removed from the material at 823 K for 3 h, first under N_2 flow (120 mL min^{-1}) and subsequently under

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O_2 flow (120 mL min^{-1}). SiO_2 is a commercial sample of non-ordered mesoporous silica obtained from Grace. Purely all silica BEA zeolite was kindly synthesized by the "Laboratoire des Matériaux Minéraux, UMR 7016, Mulhouse, France."

Surface Modification with Hexamethyldisilazane

The silylation of the surface SiOH groups has been performed with hexamethyldisilazane (HMDS) as reported in Scheme 1 (30).

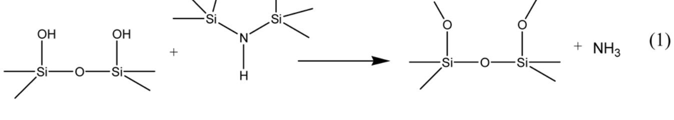
For each material, two different degrees of silylation were applied. Over MCM-41, HMDS:SiO_2 molar ratios of 0.030 and 0.250 were used for MCM-41-SilA and MCM-41-SilB, respectively (30). Over SiO_2, HMDS:silica molar ratios of 0.010 and 0.084 were used for SiO_2-SilA and SiO_2-SilB, respectively.

0.5 g of the mesoporous sample, placed in a 3-necked round-bottom flask, were heated at 573 K for 1 hour in air and then were outgassed in a primary vacuum system (ca. 10^{-3} mbar) for 2 hours at the same temperature. The activated sample was cooled at room temperature under vacuum and placed under a nitrogen atmosphere. On the top of the flask a reflux condenser system was adapted. Then 20 mL of anhydrous toluene (over 3A molecular sieves) were added under argon with a syringe together with x mL of HDMS (Aldrich, 99%), where x depends on the desired silylation degree. The system was heated at 383 K for 3 hours under reflux. The silylated sample was recovered by filtration, washed with anhydrous toluene and dried at room temperature.

Physico-Chemical Characterization

Carbon content analyses were performed on a Thermoquest NA2100 analyzer. Thermal analysis was performed on a TA Instruments (SDT600). 9 mg of sample were kept under a constant flux of air (100 mL · min^{-1}) and using a temperature ramp of 3 K · min^{-1}. The weight loss was recorded between 313 and 1173 K. Nitrogen adsorption-desorption isotherms were measured at 77 K using an ASAP 2010 instrument (Micromeritics). Before the measurement, the samples were outgassed in secondary vacuum at 573 K for 12 hours. Mesoporous volume and external surface were obtained from t-plot curves. Pore size distributions were obtained using the BJH model.

The water isotherms were performed at 298 K by thermogravimetry using a SETARAM microbalance. Prior to the sorption measurements, the samples (ca. 30 mg) were outgassed under secondary vacuum (ca. 10^{-6} mbar) at 623 K for 12 hours and cooled down to 298 K. The pressure of the sorbate was then increased step by step in order to obtain the entire adsorption isotherm. For each uptake, the equilibrium was reached and the mass recorded versus time. Adsorption isotherms were analyzed by the BET equation to calculate a quantitative assessment of the surface of the samples.



SCH. 1. Silylation reaction.

The competitive water/toluene and water/chlorobenzene adsorption experiments have been carried out in a fixed-bed adsorber at 308 K coupled to a Varian Star 3900 gas chromatograph (GC) equipped with a TCD detector. Procedures used are identical to those described by Weitkamp et al. (27,28). 100 mg of sample were activated at 573 K under dry air flow for 12 hours. After cooling, the sample was thermostated at 308 K. A constant helium flow (10 mL.min^{-1}), saturated with water and toluene (or chlorobenzene) vapors was passed through a fixed bed adsorber (downstream). Water and toluene (or chlorobenzene) vapor pressures were 5.6 kPa and 6.2 kPa (or 2.7 kPa), respectively. The sample mass used for the breakthrough experiment was 0.1 g. Tubings and valves were heated at 353 K to prevent any gas condensation. The effluent from the adsorber was periodically analyzed on-line by a Varian 3900 Gas Chromatograph (GC) equipped with a thermal conductivity detector. Corrections in the time scale were made to take account of the volume between the adsorber exit and the loop of the GC sampling valve. The amounts of water and toluene adsorbed are obtained by the breakthrough curve integration.

The sample hydrophobicity has been evaluated by the calculation of the Hydrophobicity Index (HI) as defined by Weitkamp et al. (27,28). HI value is the ratio $X_{toluene}/X_{water}$, where X is the weighted fraction of water or toluene adsorbed by the material.

The surface silanol density, N_{SiOH} (silanol number per squared nanometer) was computed assuming that the water monolayer corresponds to one molecule per hydroxyl group (31):

$$N_{SiOH} = \frac{N_{mono} \cdot N_A}{A_{BET} \cdot 10^{18}} \qquad (1)$$

In relation (1), N_{mono} is the water monolayer capacity (mol · g^{-1}), A_{BET} the surface area evaluated from the nitrogen isotherm ($m^2 \cdot g^{-1}$) and N_A the Avogadro's number.

RESULTS AND DISCUSSION

Physico-Chemical and Textural Characterizations

The physico-chemical and textural properties of the samples are reported in Tables 1 and 2. The surface coverage and the density of $Si(CH_3)_3$ groups (TMS) are

TABLE 1
Carbon analysis and surface coverage by trimethylsilyl groups (TMS)

Samples	Carbon content[a] wt.%	TMS density nm^{-2}	TMS coverage %
MCM-41	0	0	0
MCM-41-SilA	3.06	0.55	26
MCM-41-SilB	8.55	1.83	87

[a] From TGA analysis.

calculated from the carbon content and the BET area (Table 2) assuming that the surface occupied by the TMS group is $0.476\,nm^2$ (7,32). Two kinds of samples have been obtained: one partially silylated (-SilA) and one highly silylated (−SilB).

The nitrogen adsorption and desorption isotherms at 77 K are shown in Fig. 1. The condensation of nitrogen in the primary mesopore takes place at a relative pressure of about $P/P_0 = 0.30$ for non-silylated MCM-41 and partially silylated MCM-41-SilA samples, whereas it occurs slightly earlier ($P/P_0 = 0.25$) for the highly silylated MCM-41-SilB sample. The jump is reversible for all the MCM-41 samples and becomes less pronounced when the surface coverage increases. Furthermore, silylation induces a clear decrease of the total mesoporous volume and the primary mesopore size for MCM-41 samples (Fig. 1 and Table 2). The primary mesopores are the uniform cylindrical pores of MCM-41 whereas all others are the secondary mesopores which are larger (ca. 35 nm). The silylation has no noticeable effect on their diameter. The maximum lateral extension of a TMS group is roughly 0.37 nm (33). Assuming a TMS monolayer for fully silylated samples, the mesopores diameter should be reduced of 0.74 nm. The effective reduction for MCM-41-SilB is 0.6 nm, indicating that the TMS groups do not form a uniform monolayer at the primary mesopore surface. The primary mesopore coverage is not completely achieved and the TMS groups can also be grafted in the secondary mesopores.

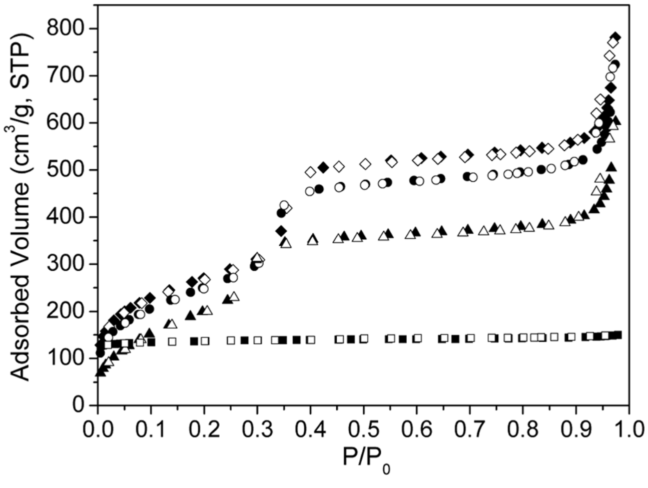


FIG. 1. Adsorption isotherm of nitrogen for MCM-41 ((), MCM-41-SilA ((), MCM-41-SilB (() and all silica BEA (() at 77 K. Filled and opened symbols correspond to adsorption and desorption branch, respectively.

The stability of the grafted TMS groups has been evaluated by TGA analysis. The TGA curves can be divided into three parts and two for the silylated samples and the nonsilylated one, respectively (Fig. 2a). For all the samples, the first step between 303 K and 373 K is assigned to the elimination of water molecules physisorbed at the mesopore surface. The amplitude of such a step is proportional to the TMS group surface coverage (Fig. 2b). Furthermore, this step is not observed for MCM-41-SilB indicating a very poor water-adsorption character for these two samples. These results are in accordance with those presented

TABLE 2
Textural properties of non-silylated and silylated samples

Samples	BET area ($m^2.g^{-1}$)	External area[a] ($m^2.g^{-1}$)	V_{total}[b] ($cm^3.g^{-1}$)	V_{meso}[c] ($cm^3.g^1$)	V_{micro}[d] ($cm^3.g^{-1}$)	Primary mesopore diameter[e] (nm)	Secondary mesopore diameter[e] (nm)
MCM-41	972	95	1.210	0.741	–	3.2	35.0
MCM-41-SilA	926	97	1.120	0.667	–	2.9	35.0
MCM-41-SilB	783	84	0.933	0.503	–	2.6	35.0
SiO_2 (Grace)	300	99	1.381	1.205	0.034	17.4	–
All silica BEA	547	10	0.231	0.024	0.207	–	–

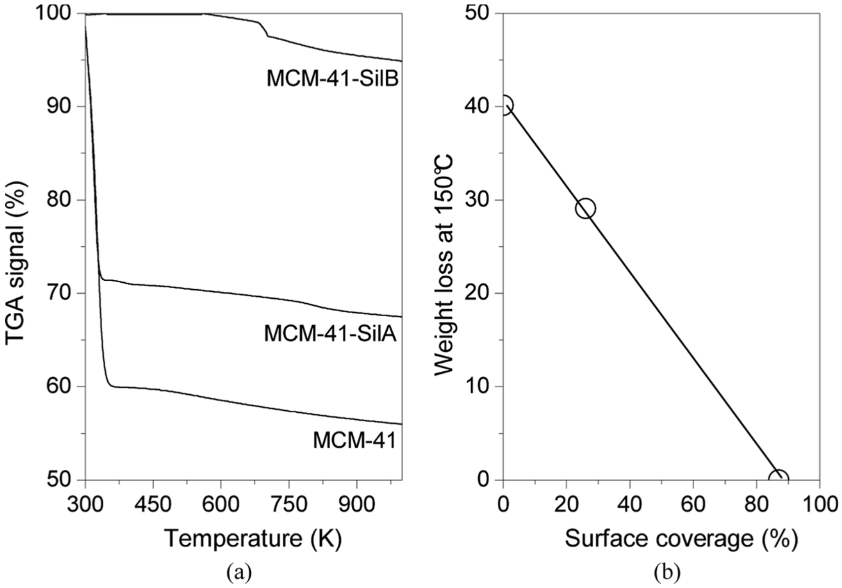
[a] estimated from the *t*-plot plateau slope.

[b] estimated at the relative pressure value of $P/P_0 = 0.97$.

[c] estimated from *t*-plot plateau y-intercept.

[d] estimated from *t*-plot by y-intercept of the linear regression calculated from t values between 0.44 and 0.74 nm.

[e] estimated from the BJH desorption plots.



(a) (b)

FIG. 2. TGA profiles (a) and weight loss (%) at 150°C as a function of TMS surface coverage (b) for the non-silylated and silylated MCM-41 samples.

by Corma et al. in case of Ti-MCM-41 samples (32). The little step around 673 K, clearly visible MCM-41-SilB corresponds to the TMS group degradation. The very slow decrease observed for all the samples between 423 K and 1073 K corresponds to irreversible water loss from dehydroxylation of surface silanols. The slope of this decrease becomes more important after 723 K, which is generally considered the best temperature to obtain a maximum density of free silanols (6).

Water Adsorption Isotherms

The water adsorption isotherms are reported in Fig. 3 for MCM-41 samples and all silica BEA zeolite. Nonsilylated MCM-41 water isotherm exhibits a significant water molecule condensation at high relative pressures. Silylation reduces this condensation drastically. The absence of condensation points on the adsorption branch for silylated MCM-41 samples indicates that the TMS groups are enough to dilute the hydroxyl sites remaining on the mesopore walls and to avoid the water liquid meniscus formation, which is necessary to the condensation process. In order to compare the different solids, the monolayer water content has been calculated for all the samples from the BET equation. The values of surface silanol density calculated by Eq. (1) are reported in Table 3 for all the samples. In order to validate the model used, the same calculation has been done for a commercial amorphous silica sample (GRACE). The calculated value of 4 hydroxyls per nm^2 is in agreement with the value of 4.6 found by Zhuravlev (34) for amorphous silica. The value for the

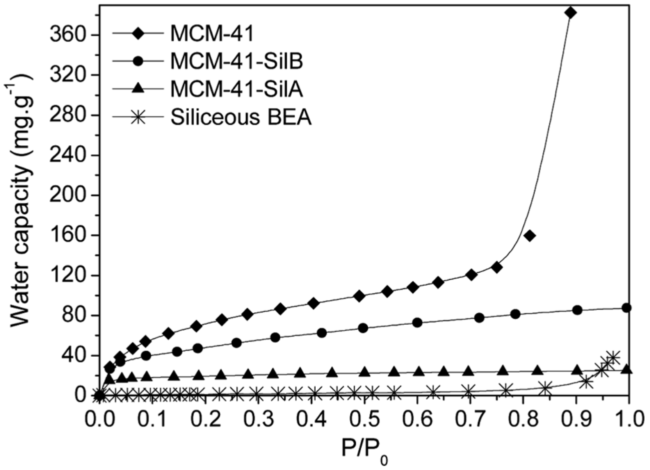


FIG. 3. Water adsorption isotherms at 294 K for MCM-41 and for all silica BEA zeolite.

TABLE 3
Surface and adsorption properties of silylated and non-silylated samples

Samples	Silanol density SiOH.nm^{-2}	Water capacity (mg.g^{-1})	Toluene capacity (mg.g^{-1})	HI
MCM-41	2.2	74.5	644	8.6
MCM-41-SilA	1.4	35.6	593	16.7
MCM-41-SilB	0.7	14.9	534	35.8
SiO_2 (Grace)	4	59.1	314	5.3
All silica BEA	0.1	12.6	231	18.3

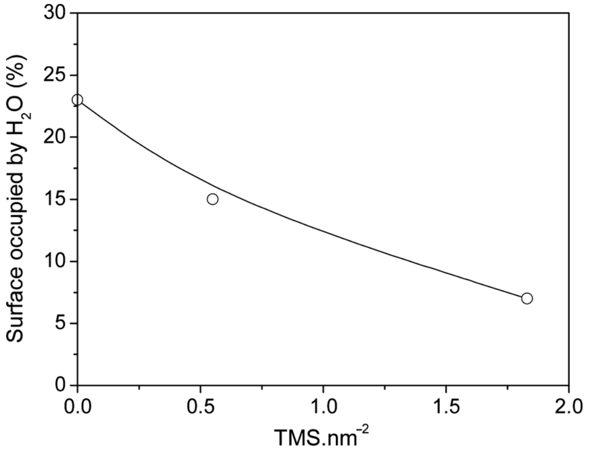


FIG. 4. Surface percentage occupied by water molecules as a function of TMS group density for MCM-41 samples.

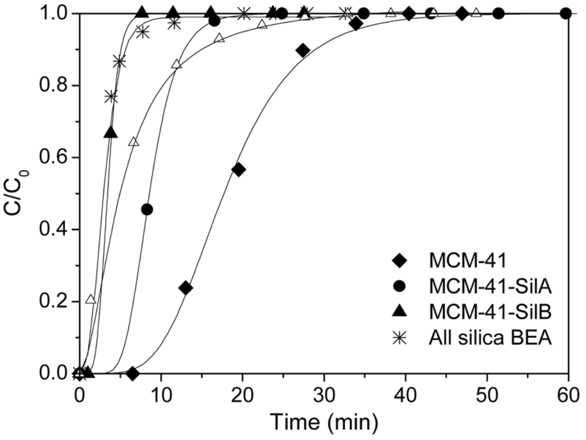


FIG. 5. Water Breakthrough curves obtained from water – toluene (or chlorobenzene, open symbols) competitive adsorption for MCM-41 and for, all silica BEA zeolite samples.

MCM-41 sample is lower (2.2 per nm^2) but comparable to the values obtained by other authors (13,7,35,36) (0.7 to 3 hydroxyls per nm^2). Silylation induces for all the samples a hydroxyl group decrease.

In order to give a deeper insight into the extent of the mesoporous volume occupation by water molecules for the two solids, Fig. 4 represents the percentage of BET surface occupied by water molecules as a function of TMS group density. The surface occupied by water molecules has been calculated fitting the linear region (relative pressure range: 0.05–0.2) of the water isotherm by the BET equation and assuming that the molecular cross-sectional area of the water molecule is 10.5 Å^2 (37). As expected, the extent of the surface occupied by water is directly correlated to the silylation degree and it decreases as the silylation degree increases.

Competitive Adsorption of Water–Toluene Vapors and HI Determination

The water and toluene breakthrough curves are shown in Figs. 5 and 6, respectively. Water and toluene capacities, computed from the breakthrough curve integration, are reported in Table 3. For the MCM-41 samples, the water breakthrough times and consequently the water loading decrease when the silylation degree increases (Fig. 5). Furthermore, water breaks through before toluene, indicating an organophilic character for MCM-41 solids. However, no water displacement by toluene occurs, as it was observed by Gläser and co-workers for aluminium-containing MCM-41 materials (23). No water mesopore condensation is observed whatever the sample and its silylation degree. Toluene capacity decreases when the silylation degree increases (Fig. 6 and Table 3). This decrease can be explained by mesoporous volume decrease due to the silylation, indicating that toluene molecules adsorbed preferentially in the primary mesopores. Furthermore, the jump after the plateau observed on the toluene breakthrough curve for MCM-41-SilB sample (Fig. 6) results from toluene capillary condensation inside the mesopores. Thus, for highly silylated samples the high relative humidity does not avoid large toluene mesopore filling. In this case, the water molecules also adsorbed are certainly very dispersed in the primary mesopores or preferentially adsorbed in the second ones. Water cluster formed on isolated silanols does not prevent the toluene multilayer formation necessary for the capillary condensation for MCM41-silB. For the nonsilylated or the less silylated (MCM41-silA) samples, water clusters are certainly larger and near from each other in order to avoid toluene capillary condensation phenomenon. HI values calculated

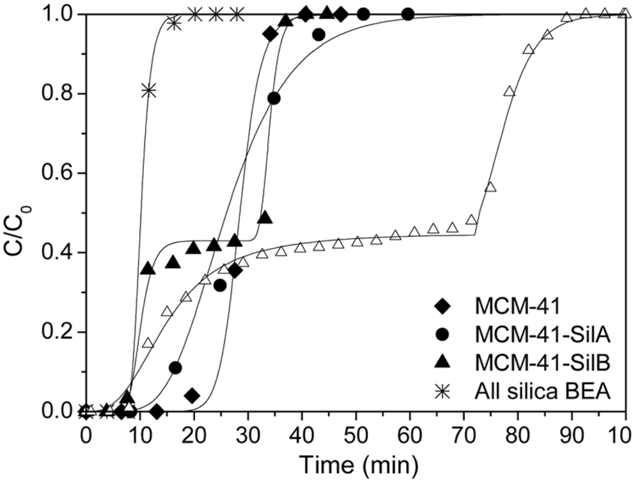


FIG. 6. Toluene (or chlorbenzene, open symbols) breakthrough curves obtained from water – toluene (or chlorobenzene, opened symbols) competitive adsorption for MCM-41 and all silica BEA zeolite.

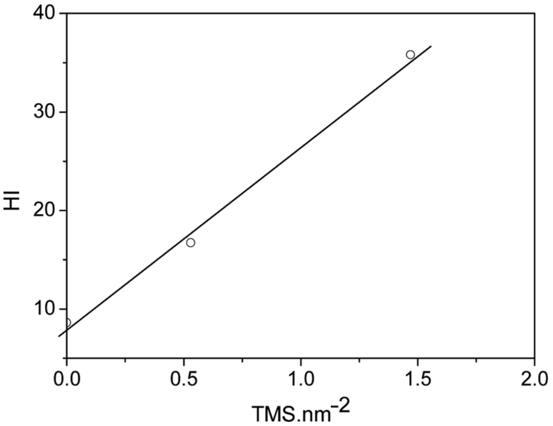


FIG. 7. Correlation between hydrophobicity index and TMS surface density obtained by grafting.

from the breakthrough curves have been reported in Table 3. A linear correlation can be established between HI values and grafting (Fig. 7). Thus, the MCM-41 hydrophobicity seems to be directly correlated to the elimination of the silanol groups on which water molecules are preferentially adsorbed. The HI index has been extensively used by Weitkamp (23,27,28,38) and other authors (39,42) to described the hydrophobicity in acidic zeolites. The correlation between the HI index and the Al content (or Bronsted site concentration) have been found (41,42) indicating a preferential water adsorption on bridged hydroxyl groups (SiOHAl). So in both cases (zeolites and MCM-41), the HI index can be directly related with the surface chemistry: water chemisorption on Bronsted sites and on remaining silanols for zeolites and MCM-41 materials, respectively. The value obtained for the nonsilylated MCM-41 is not the same as the value mentioned by Calleja et al. (40). This indicates that the synthesis experimental conditions as Calleja et al. have already underlined play an important role on MCM-41 hydrophobic and hydrophilic properties (15,40).

Comparison Between the VOC Adsorption Behavior onto a Hydrophobic All Silica Microporous Material (BEA Zeolite) and a Hydrophobic Mesoporous Material (MCM-41-SilB)

The all silica BEA zeolite is known to be a very hydrophobic molecular sieve with a type III water adsorption isotherm (Fig. 3) and a relatively high HI value (18.3) compared to HBEA zeolites with high Si/Al ratio (41,42). Its high hydrophobicity results from low silanol density (0.1 SiOH $\cdot$nm^{-2}, Table 3) due to the large crystallite size and a low defect content (silanol nests). The same observation has also been made for silicalite I (all silica MFI) (43). The water isotherm of the highly silylated MCM-41-SilB sample suggests that this sample is more hydrophilic than the zeolitic material. Actually, the monolayer water capacities calculated from the isotherm fitting with the BET model (relative pressure range: 0.05–0.2) are 1.1 mg.g^{-1} and 16.3 mg.g^{-1} for all silica BEA and MCM-41-SilB, respectively. However, toluene adsorption isotherms reported in Fig. 8 are totally reversible and characteristic of the porosity of the two samples (type I for zeolite and type IV for MCM-41-SilB). The toluene capacity is limited by the available porous volume of the two solids. For the two materials, the volumes occupied by toluene, calculated by assuming that the adsorbed phase has the normal bulk liquid density (0.866 g.cm^{-3}), are quite close but lower to the microporous or mesoporous volumes calculated from nitrogen adsorption isotherm at 77 K (Table 2). For all silica BEA zeolite, toluene molecules occupy 84% of the microporous volume against 82% of the mesoporous volume for MCM-41-SilB. The same observation could be done for chlorobenzene adsorption onto MCM-41-SilB (Fig. 8, opened symbols). Chlorobenzene molecules are able to occupy up to 90% of the mesopororous volume. Furthermore, the capillary condensation takes place at lower relative pressure values for chlorobenzene adsorption. These two observations indicate a more efficient mesopore filling by chlorobenzene than toluene. It could result from higher adsorbate – adsorbate interactions in case of chlorobenzene molecule due to their higher polarizability.

The competitive adsorption of toluene and water vapors at 308 K reveals that water is adsorbed in the rather the same quantities for the two materials (Fig. 6a and Table 3) even though silanol density is higher for MCM41-SilB sample. The toluene capacity is enhanced for the MCM-41-SilB sample (2.3 times higher). From this observation, it results in a higher HI value for

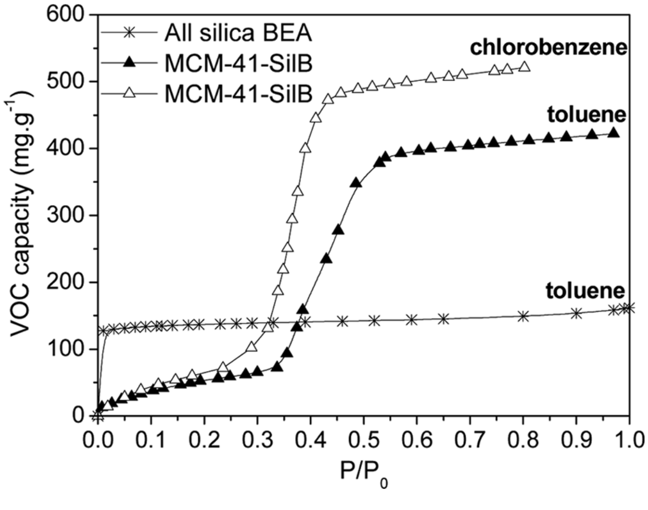


FIG. 8. Toluene and chlorobenzene adsorption isotherms at 294 K for MCM-41-SilB and all silica BEA zeolite.

MCM-41-SilB (35.8) sample than for all silica BEA (18.3). In case of MCM-41-SilB, the large available porous volume counter-balances easily the relatively high silanol density. If toluene is replaced by chlorobenzene which is slightly more polar and less volatile, the amount adsorbed (5.4 mmol.g^{-1}) in the same experimental conditions (308 K, 10 mL.min^{-1}) is nearly the same. Even if the breakthrough curve profile is the same for the two sorbates, the area delimitated by the breaktrough curve is 2 times higher for chlorobenzene than for toluene experiment. This difference is not surprising and is explained by a lower chlorobenzene vapor pressure at 308 K (2.7 kPa). Furthermore, the water content is nearly 2 times higher in competitive chlorobenzene adsorption than in the toluene one. This result is probably due to the chlorobenzene polarity. The water molecule could interact with chlorobenzene via the hydrogen bond formed between the water H atom and the Cl atom. In this case, chlorobenzene adsorption enhances via H-bond water adsorption inside the mesopores. Nevertheless, the organic molecule is preferentially adsorbed. This result highlights the relevant organophilicity of the highly silylated MCM-41 material, since organic molecules, even polar, are adsorbed by far more preferentially than water when they are in competition with it.

CONCLUSIONS

The present study shows that the hydrophobic properties MCM-41 materials can be tuned and enhanced by grafting trimethylsilyl moieties. The hydrophobicity increases linearly with the silylation degree. Thus, hydrophobic properties can be tuned by controlling the silylation agent quantity for MCM-41 materials. Furthermore, the extended silylation of the mesopore inner surface in MCM-41 has enhanced its organophilicity: the capillary condensation of toluene in the mesopores (even in presence of water) is preserved whereas it is eliminated for water. MCM-41-SilB has a HI value 2.3 times higher than a hydrophobic zeolite (purely all silica BEA) and it can therefore be considered a particularly efficient adsorbent. Thanks to an important porous volume, highly silylated MCM-41 sample offers larger capacities for COV adsorption even under 100% of relative humidity than hydrophobic zeolites when capillary water condensation is eliminated by organophilic grafting.

The fine tuning of the hydrophilic/hydrophobic character and the quantification of these properties by HI determination are relevant features to be considered in the preparation of mesoporous materials. Such an approach can find applications in the production of these kinds of solids as catalysts, adsorbents, inorganic fillers of hybrid/composites, and so on.

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