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Adsorption of Hydrocarbons on Mesoporous SBA-15 and PHTS Materials

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Plugged hexagonal templated silica (PHTS) materials are synthesized using a high TEOS/$EO_{20}PO_{70}EO_{20}$ ratio in the SBA-15 synthesis. This generates internal microporous nanocapsules or plugs in part of the channels, which could be inferred from the two-step desorption branch. These materials exhibit a tunable amount of open and plugged pores and a very high micropore volume (up to 0.24 mL/g) and are more stable than the conventional micellar templated structures known so far. In this study the adsorption properties of PHTS are investigated and compared to those of its plug-free analogue SBA-15. For this purpose nitrogen, *n*-hexane, *n*-heptane, *c*-hexane, 3-methylpentane, 1-hexene, and water were adsorbed on SBA-15 and PHTSs with a different ratio of open and plugged mesopores. The adsorption of *n*-hexane, *c*-hexane, *n*-heptane, and 3-methylpentane on SBA-15 and PHTS-A demonstrated that the presence of the plugs had an effect on the uptake of adsorbate in the low relative pressure region, the position of the capillary condensation step, and the total adsorbed amount of adsorbate. The results showed that *n*-heptane and 3-methylpentane cannot access part of the micropore system of SBA-15 and PHTS-A. Adsorption of *c*-hexane and *n*-hexane on PHTS-A indicated that not only the kinetic diameter but also the shape of the molecule is an important factor for being able to be adsorbed into the micropores or past the plugs. Moreover, these two adsorbates were the most efficient in filling up the available pore volume. From the adsorption of *n*-hexane on PHTSs with a different ratio of open and plugged pores, it was concluded that the size of the plugs differed, which depends on the synthesis conditions. Water adsorption isotherms proved SBA-15 and PHTS-B to be more hydrophobic than PHTS-A. *n*-Hexane, 1-hexene, and toluene were adsorbed on SBA-15 and the PHTSs to investigate the influence of the polarity of the adsorbate. The isotherms showed higher uptakes for polar adsorbates on more hydrophobic materials and vice versa.

Introduction

The introduction of the M41S family of ordered mesoporous materials in the early 1990s[1] stimulated the development of other types of this new class of materials. In 1998 SBA-type materials were synthesized[2] of which SBA-15 has attracted a lot of attention because of its remarkable features. SBA-15 consists of a 2-D hexagonally ordered array of long, interconnected pore channels with diameters that can vary within the range of 4.6−30 nm[2]. Its mechanical stability is comparable to that of MCM-41 and KIT-1 materials, but its thermal and hydrothermal stability is higher compared to M41S and other materials.[3] One of the most striking properties of SBA-15 is the coexistence of meso- and micropores.[4] This material consists not only of large, uniform, and ordered mesoporous channels but also of micropores and smaller mesopores which provide connectivity between the mesochannels. The presence of the micropores arises from the penetration of the EO blocks of the surfactant ($EO_{20}PO_{70}EO_{20}$) into the silica wall during synthesis so that microporosity is generated upon calcination.[5] Materials with combined micro- and mesoporosity can offer significant supplementary advantages such as an improved diffusion rate for transport in catalytic processes or multifunctionality to process a large variety of feedstocks.[6] For possible catalytic applications, the study of transport phenomena in the pore channels is of great interest, because the guest molecules need efficient transport channels to and from the inner surfaces of the meso and micropores so that they can react and afterward leave the pores. In this way the catalytic power of a material is closely related to the transport process of the guest molecules through the pores.[7] Catalytic studies have been performed on SBA-15 modified with among others catalytically active Ru,[8] Al,[9] arenesulfonic groups,[10] V,[11] Ti,[12] Zr,[13] Co,[14] Fe,[15] and Ni−

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(1) Kresge, C. T.; Leonowics, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Frederickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

(3) Cassiers, K.; Linssen, T.; Mathieu, M.; Benjelloun, M.; Schrijnemaekers, K.; Van Der Voort, P.; Cool, P.; Vansant, E. F. *Chem. Mater.* **2002**, *14*, 2317.

(4) Ryoo, R.; Ko, C. H.; Kruk, M.; Antochshuk, V.; Jaroniec, M. *J. Phys. Chem. B* **2000**, *104*, 11465.

(5) Kruk, M.; Jaroniec, M.; Ko, C. H.; Ryoo, R. *Chem. Mater.* **2000**, *12*, 1961.

(6) Van Der Voort, P.; Ravikovitch, P. I.; de Jong, K. P.; Benjelloun, M.; Van Bavel, E.; Janssen, A. H.; Neimark, A. V.; Weckhuysen, B. M.; Vansant, E. F. *J. Phys. Chem. B* **2002**, *106*, 5873.

(7) Gedat, E.; Schreiber, A.; Albrecht, J.; Emmler, Th.; Shenderovich, I.; Findenegg, G. H.; Limbach, H.-H.; Buntkowsky, G. *J. Phys. Chem. B* **2002**, *106*, 1977.

(8) Joseph, T.; Deshpande, S. S.; Halligudi, S. B.; Vinu, A.; Ernst, S.; Hartmann, M. *J. Mol. Catal. A: Chem.* **2003**, *206*, 13.

(9) Yue, Y.; Gédéon, A.; Bonardet, J.-L.; Melosh, N.; D'Espinose, J.-B.; Fraissard, J. *Chem. Commun.* **1999**, 1967.

(10) Melero, J. A.; Stucky, G. D.; van Grieken, R.; Morales, G. *J. Mater. Chem.* **2002**, *12*, 1664.

(11) Fornés, V.; López, C.; López, H. H.; Martínez, A. *Appl. Catal., A* **2003**, *249*, 345.

(12) Zhang, W.-H.; Lu, J.; Han, B.; Li, M.; Xiu, J.; Ying, P.; Li, C. *Chem. Mater.* **2002**, *14*, 3413.

(13) Landau, M. V.; Titelman, L.; Vradman, L.; Wilson, P. *Chem. Commun.* **2003**, 594.

(14) Martínez, A.; López, C.; Márquez, F.; Díaz, I. *J. Catal.* **2003**, *220*, 486.

(15) Nozaki, C.; Lugmair, C. G.; Bell, A. T.; Don Tilley, T. *J. Am. Chem. Soc.* **2002**, *124*, 13194.

B.[16] On the other hand studies of adsorption of organics on SBA-15 are limited. Newalker et al.[17,18] studied the utility of SBA-15 to separate C_2 and C_3 saturated and unsaturated hydrocarbons. The results clearly demonstrated the importance of framework microporosity in olefin uptake on SBA-15 materials.[18] A study of the mechanical stability of SBA-15 was performed using N_2, benzene, and *n*-heptane adsorption on compressed materials.[19] It was found that part of the micropores were not accessible for larger organics such as benzene and *n*-heptane. The benzene selectivity over toluene for SBA-15 and SBA-16 materials was investigated by Ueno et al.[20] Gedat et al.[7] studied the confinement of benzene-d_6 in SBA-15 and compared it to bulk benzene-d_6. Finally, a thermodynamical study of the pore filling of *n*-hexane in MCM-41 and SBA-15 with varying pore diameters was also performed.[21]

Recently another type of combined micro- and mesoporous material was developed, namely, PHTS or plugged hexagonal templated silica.[6] The use of a high TEOS/EO_{20}-$PO_{70}EO_{20}$ ratio in the SBA-15 synthesis generates internal microporous nanocapsules or plugs in part of the channels, which could be inferred from the two-step desorption branch.[6] These materials exhibit a tunable amount of open and plugged pores and a very high micropore volume (up to 0.24 mL/g) and are more stable than the conventional micellar templated structures known so far.[6,22] These features make this material very promising toward applications.

The main objective of the present study is to investigate the adsorption properties of PHTS and compare them with the results of its plug-free analogue, namely, SBA-15. In addition the effect of a different ratio of open and plugged pores will be investigated. As adsorbates linear (*n*-hexane and *n*-heptane), branched (3-methylpentane), cyclic (*c*-hexane), aromatic (toluene), and unsaturated (1-hexene) hydrocarbons will be used. Finally, the hydrophilicity of the PHTS and SBA-15 will be investigated through water adsorption. Through this information more insight will be gained in the influence of the presence, the size, the location, and the nature of the plugs within the mesoporous channels on the adsorption of hydrocarbons.

Experimental Section

Synthesis. SBA-15 was synthesized as follows: 4 g of P123 ($EO_{20}PO_{70}EO_{20}$, Aldrich) was dissolved in 30 g of water and 120 g of a 2 M HCl solution with stirring at 45 °C. Then 8.5 g of TEOS (tetraethoxysilane, 98% Acros) was added. The resulting mixture was stirred for 8 h at 45 °C and aged overnight under static conditions at 80 °C. PHTS materials were prepared as follows: 4 g of P123 was dissolved in 30 g of water and 120 g of a 2 M HCl solution with stirring at a fixed temperature of 60 °C (PHTS-A) or 70 °C (PHTS-B). Then 18 g of TEOS (TEOS/P123 = 125) was added. The resulting mixture was stirred for 8 h at 60 °C (PHTS-A) or 70 °C (PHTS-B) and aged overnight under static conditions at 80 °C.

(16) Chen, X.; Hu, H.; Liu, B.; Qiao, M.; Fan, K.; He, H. *J. Catal.* **2003**, *220*, 254.

(17) Newalker, B. L.; Choudary, N. V.; Kumar, P.; Komarneni, S.; Bhat, T. S. G. *Chem. Mater.* **2002**, *14*, 304.

(18) Newalker, B. L.; Choudary, N. V.; Turaga, U. T.; Vijayalakshmi, R. P.; Kumar, P.; Komarneni, S.; Bhat, T. S. G. *Chem. Mater.* **2003**, *15*, 1474.
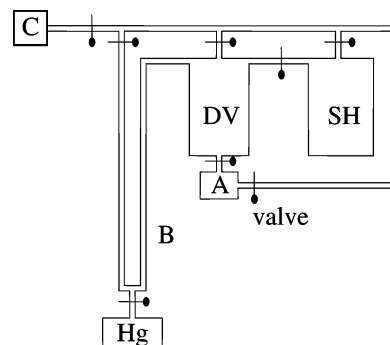
(19) Hartmann, M.; Vinu, A. *Langmuir* **2002**, *18*, 8010.

(20) Ueno, Y.; Tate, A.; Niwa, O.; Zhou, H.-s.; Yamada, T.; Honma, I. *Chem. Commun.* **2004**, 746.

(21) Trens, P.; Tanchoux, N.; Maldonado, D.; Di Renzo, F.; Fajula, F. *Proceedings of the 14th International Zeolite Conference*, Cape Town, South Africa, 2004; p 1812.

(22) Van Bavel, E.; Cool, P.; Aerts, K.; Vansant, E. F. *J. Phys. Chem. B* **2004**, *108*, 5263.

Chart 1.   Volumetric Sorption Apparatus[a]

[a] A, adsorptive holder; B, manometer; C, vacuum pump; DV, dead volume; SH, sample holder.

Table 1. Structural Characteristics of SBA-15 and PHTS Samples[a]

sample	D (Å)	S_{BET} (m²/g)	V_{micro} (cm³/g)	V_{total} (cm³/g)	V_{open} (cm³/g)	$V_{plugged}$ (cm³/g)	V_o/V_{pl}
SBA-15	68	685	0.13	0.75	0.62		
PHTS-A	68	691	0.17	0.62	0.16	0.29	0.55
PHTS-B	68	649	0.14	0.64	0.25	0.25	1.00

[a] Notation: D, pore diameter from the adsorption branch; S_{BET}, BET specific surface area; V_{micro}, micropore volume; V_{total}, total pore volume; $V_{open\ mesopores} = V_{total} - V_{first\ step\ desorption\ branch}$; $V_{plugged\text{-}mesopores} = V_{total} - V_{open} - V_{micro}$; $V_o/V_{pl} = V_{open\ mesopores}/V_{plugged\ mesopores}$.

Characterization. Porosity and surface area studies were performed on a Quantachrome Autosorb-1-MP automated gas adsorption system using nitrogen as the adsorbate at liquid nitrogen temperature (77 K). All samples were outgassed under vacuum for 16 h at 200 °C before adsorption measurements. The pore diameter was obtained from the nitrogen adsorption branch using the Barrett–Joyner–Halenda (BJH) method. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method, and the micropore volume was calculated using the *t*-plot method.

The hydrocarbon and water adsorptions were performed on a homemade and classical adsorption apparatus (Chart 1) at room temperature (20 °C ± 1 °C). All samples were outgassed under vacuum for 16 h at 200 °C before adsorption measurements. In the calculation of the amount of adsorbed adsorbate, the vapor pressure (P_0) was adjusted by the saturator temperature. The equilibration time was checked at various relative pressures. The ultimate equilibration time used to record the adsorption isotherm was larger than the minimum equilibration time observed for the various relative pressures.

The dipole moments of 1-hexene and toluene were calculated using the B3LYP/6-311G** quantum chemical method.

Results and Discussion

The results of nitrogen sorption on the SBA-15 and PHTS materials used in this study are displayed in Table 1. Materials with the same pore diameter were chosen to avoid differences in the position of the capillary condensation step of the adsorbates. The nitrogen sorption isotherms of the SBA-15 and PHTS samples can be seen in Figures S1–S3 of the Supporting Information.

Comparison of the Adsorption Behavior of SBA-15 and PHTS-A. First the adsorption of *n*-hexane, *c*-hexane, 3-methylpentane, and *n*-heptane on SBA-15 and PHTS-A will be discussed. In Figures 1 and 2, the adsorption isotherms of these adsorbates on these materials are displayed together with the adsorption isotherm of nitrogen for comparison. All isotherms are of type IV. The difference between the uptakes of organics and nitrogen on both materials is significant. This discrepancy is due to the size difference of the organics and nitrogen
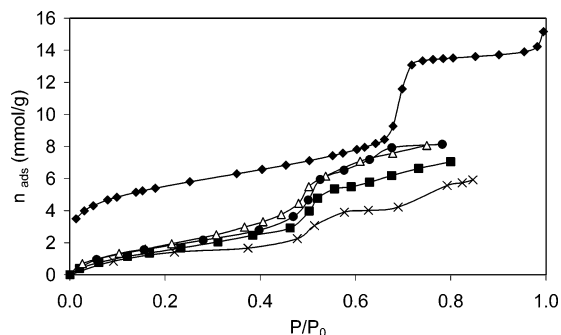
Figure 1. Adsorption isotherms of nitrogen (♦) (at 77 K), *c*-hexane (■), *n*-hexane (△), *n*-heptane (×), and 3-methylpentane (●) (all at room temperature) on SBA-15.
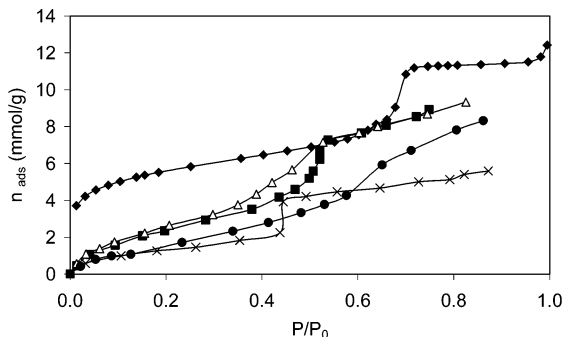

Figure 2. Adsorption isotherms of nitrogen (♦) (at 77 K), *c*-hexane (■), *n*-hexane (△), *n*-heptane (×), and 3-methylpentane (●) (all at room temperature) on PHTS-A.

and the structure of the adsorbed layer.[23] After the capillary condensation step there is still a continual adsorption (Figure 3a–d). Because the adsorptives are much larger than N_2, they are not piled as efficiently as N_2. This leaves some room for other molecules to adsorb even after capillary condensation has already occurred.

A comparison of the adsorption isotherms of *n*-hexane, *c*-hexane, 3-methylpentane, and *n*-heptane on SBA-15 and PHTS-A in Figures 1 and 2 shows that the presence of the plugs has an effect on the adsorption behavior of the different adsorbates. In the low relative pressure region, the uptake of organics on SBA-15 is approximately the same for all adsorbates whereas on PHTS-A there is a difference in *c*-hexane and *n*-hexane uptake on one hand and 3-methylpentane and *n*-heptane uptake on the other. Moreover, there is a clear difference in the position of the capillary condensation step between SBA-15 and PHTS-A for some of the adsorbates.

The plugs of PHTS are formed using a high TEOS/EO_{20}-$PO_{70}EO_{20}$ ratio in the SBA-15 synthesis. A part of TEOS can interact with the EO chains of the template and undergo accelerated hydrolysis and condensation forming the mesochannels. The excess amount of TEOS can be partially or completely solubilized in the PO micellar core, wherein the silica species can slowly undergo hydrolysis and condensation leading to the formation of the plugs.[29] The plugs themselves are microporous,[6] and their microporosity increases with increasing synthesis temperature.[22] An open mesopore is formed when a plug is present at only one side of a pore; a plugged mesopore is the pore section between two plugs. More detailed information about the structure, sorption behavior, and influence of the synthesis conditions of PHTS can be found in refs 6 and 22.

The influence of the plugs on the adsorption behavior of the adsorbates arises from the fact that a plug locally narrows a mesopore so that a molecule can experience diffusional limitations. From that it can be inferred that the kinetic diameter of the molecule and the size of the plugs will be important toward an adequate adsorption on PHTS materials. Other determining factors are the location and the nature of the plugs. If large plugs are localized in the beginning of the pores, it is likely that diffusional limitations will occur and that not all of the available pore volume will be utilized. When the plugs are however halfway into the pores, the adsorption behavior of PHTS will be comparable to that of SBA-15. Whether or not the plugs are hydrophilic can also be of influence on the adsorption behavior. Furthermore, it will be equally important to infer whether the hydrocarbons will be able to diffuse into the micropores of SBA-15 and PHTS. Publications concerning the size of the micropores are limited. Ryoo et al.[4] performed silylation on SBA-15, which indicated that a significant fraction of the complementary pores of this material exhibit sizes between 1 and 3 nm. Nossov et al.[24] used hyperpolarized ^{129}Xe NMR to investigate the micropore size as a function of the aging temperature of SBA-15. It was found that the micropores of the material synthesized at 60 °C are larger than twice the kinetic diameter of xenon ($d_{Xe} = 3.96$ Å). Finally, Ueno et al.[20] determined the micropore diameter at a median value of 6 Å using the positron annihilation technique. These factors are considered in interpreting the adsorption isotherms of the hydrocarbons on the different materials. From comparison of these isotherms, it can be concluded which factor is decisive for an adequate adsorption.

To clarify the difference in adsorption behavior between SBA-15 and PHTS-A, the adsorption isotherms of *n*-hexane, *c*-hexane, 3-methylpentane, and *n*-heptane on SBA-15 and PHTS-A are displayed together in Figure 3a–d. As can be seen from Figure 3a,b, the *c*-hexane and *n*-hexane uptake in the low relative pressure region (at $P/P_0 < 0.1$) is larger for PHTS-A than for SBA-15, whereas for 3-methylpentane and *n*-heptane (Figure 3c,d) the uptake on both materials is roughly the same. Moreover there is a difference in the position of the capillary condensation step between SBA-15 and PHTS-A. For *c*-hexane and *n*-hexane this difference is minor, and for 3-methylpentane and *n*-heptane it is major. To explain this different adsorption behavior, the kinetic diameter of the adsorbates (Table 2) and the porous characteristics of the adsorbents (Table 1) have to be considered. One of the differences between SBA-15 and PHTS-A is the micropore volume: 0.13 and 0.17 mL/g, respectively. If the adsorbates can access the micropores, a larger adsorbate uptake is expected in the low relative pressure region. Based on the kinetic diameter of the adsorbates, they should have access to the micropores according to their size, which increases in the following order: *n*-hexane = *n*-heptane < 3-methylpentane < *c*-hexane. Considering the higher micropore volume of PHTS-A and the kinetic diameters of the adsorbates together, this means that larger *n*-hexane and *n*-heptane uptakes in the low relative pressure region of PHTS are expected. This is the case for *n*-hexane, but not for *n*-heptane. *n*-Heptane adsorptions on SBA-15 were reported before,[19] from which it was concluded that part of the SBA-15 pore system was not

(23) Bambrough, C. M.; Slade, R. C. T.; Williams, R. T.; Burkett, S. L.; Sims, S. D.; Mann, S. *J. Colloid Interface Sci.* **1998**, *201*, 220.

(24) Nossov, A.; Haddad, E.; Guenneau, F.; Galarneau, A.; Di Renzo, F.; Fajula, F.; Gédéon, A. *J. Phys. Chem. B* **2003**, *107*, 12456.
(25) Long, Y.; Xu, T.; Sun, Y.; Dong, W. *Langmuir* **1998**, *14*, 6173.
(26) Chen, N. Y.; Degnan, T. F.; Smith, C. M. *Molecular Transport and Reactions in Zeolites*; VCH: New York, 1994; p 134.
(27) Breck, D. W. *Zeolite molecular sieves: Structure, chemistry and use*; John Wiley & Sons: New York, 1974.
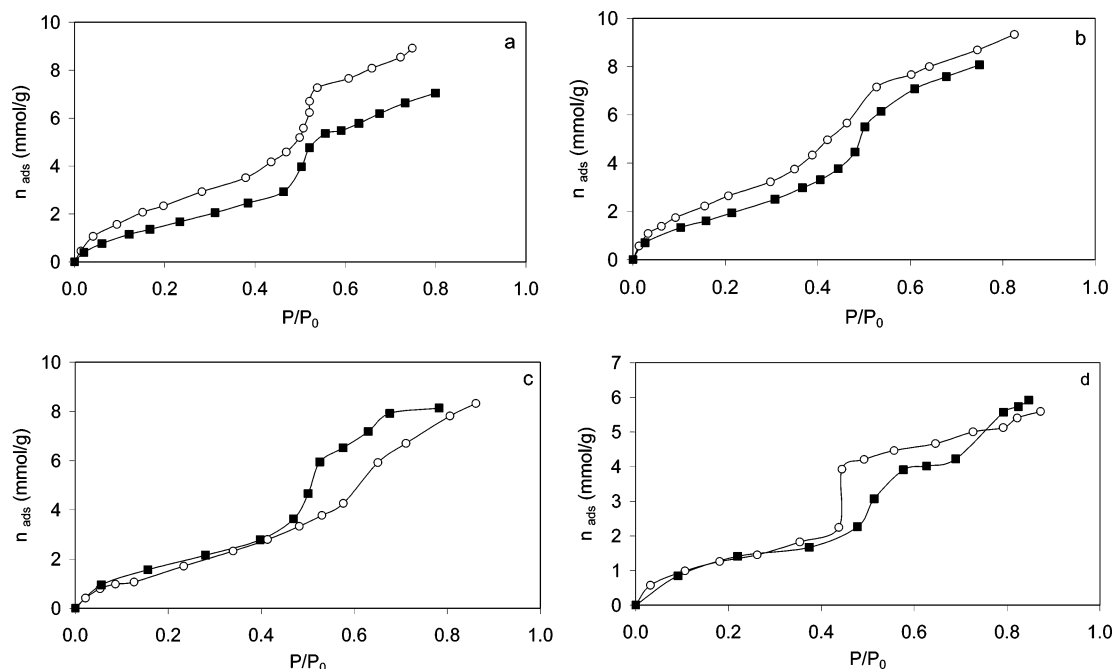
Figure 3. Adsorption isotherms of (a) *c*-hexane, (b) *n*-hexane, (c) 3-methylpentane, and (d) *n*-heptane on SBA-15 (■) and PHTS-A (○) at room temperature.

Table 2. Kinetic Diameters and Dipole Moments of the Adsorbates[a]

adsorbate	kinetic diameter (Å)	μ_D (D)
n-heptane	4.3	
n-hexane	4.3	
c-hexane	6.0	
3-methylpentane	5.0	
1-hexene	4.3	0.403
toluene	5.85	0.354

[a] References 25−27.

accessible for this alkane with a longer carbon chain. This can explain the equal *n*-heptane uptake on SBA-15 and PHTS-A in the low relative pressure region given the fact that this adsorbate cannot access part of the micropores. An analogous explanation can be given for the larger 3-methylpentane. Striking though is the higher *c*-hexane uptake for PHTS-A as compared to SBA-15 since *c*-hexane has the largest kinetic diameter of all adsorbates. The adsorption kinetics is also faster on PHTS-A (9 min) compared to SBA-15 (16 min). Because the micropore volume of PHTS-A is higher than that of SBA-15, these results indicate that *c*-hexane can be adsorbed into the micropores. The above results indicate that beside the kinetic diameter the shape of the molecule is also an important factor in determining whether a molecule can be adsorbed in a micropore.

As already mentioned before, the capillary condensation of *c*-hexane and *n*-hexane occurs around the same relative pressure on SBA-15 and PHTS-A (Figure 3a,b). Considering the fact that adsorbents with the same pore diameter (68 Å) were chosen to avoid differences in the position of the capillary condensation step, it can be concluded that the presence of the plugs has no effect on the position of this step for *n*-hexane and *c*-hexane on PHTS-A. The slopes of the capillary condensation steps of *c*-hexane on SBA-15 and on PHTS-A are comparable. Table 3 shows additional information. Here the total adsorbed amount of adsorbate on each material is displayed. These values are taken at a relative pressure of 0.7 because then all adsorbates are condensed. Table 3 shows that more *c*-hexane adsorbs onto PHTS-A (8.54 mmol/g) than on SBA-15 (6.19

mmol/g). This and the fact that the slope of the capillary condensation step on PHTS-A resembles the one of SBA-15 indicate that *c*-hexane is adsorbed in more homogeneous layers on PHTS-A, which can be related to the (symmetrical) shape of the molecule. For the linear hydrocarbons, a quite different slope of the capillary condensation step on PHTS-A is observed. The slope of the capillary condensation step of *n*-hexane on PHTS-A is slightly less steep than the one on SBA-15. *n*-Heptane on the other hand condenses faster on PHTS-A than on SBA-15 and shows a steeper slope on PHTS-A. This can be explained when the data in Table 3 are considered too. The last three columns of this table express the adsorbed amount of organic to the adsorbed amount of nitrogen in percent so that the efficiency in filling up the available pore volume can be easily deduced. The least efficient adsorbate is *n*-heptane: the available pore volume is only filled up until 32% of the capacity for SBA-15 and 41% of the capacity for PHTS-A. This low efficiency can be caused by a less efficient piling of the molecules in the channels because of the longer carbon chain of *n*-heptane. The higher adsorption efficiency of *n*-heptane on PHTS-A can be explained as follows. Due to the presence of the plugs and the longer carbon chain of *n*-heptane as compared to *n*-hexane, this molecule is probably forced to pass through the remaining pore opening at the plugs in a specific orientation. This could cause a better filling of the PHTS pore volume. As a result the capillary condensation step of *n*-heptane on PHTS-A is faster and steeper than the one of *n*-heptane on SBA-15 and the one of *n*-hexane on PHTS-A. The capillary condensation of 3-methylpentane on PHTS-A occurs at higher P/P_0 as compared to SBA-15 (Figure 3c). This can be explained through the diffusion limitations that the molecules experience at the plug so that the capillary condensation is postponed and occurs at a higher relative pressure.[28] The larger kinetic diameter of 3-methylpentane in comparison with *n*-heptane can only be part of the explanation of why this molecule

(28) Zhao, X. S.; Lu, G. Q. *J. Phys. Chem. B* **1998**, *102*, 1556.
(29) Kruk, M.; Jaroniec, M.; Joo, S. H.; Ryoo, R. *J. Phys. Chem. B* **2003**, *107*, 2205.

Table 3. Total Amount Adsorbed of Adsorbate n_{ads} at P/P_0 = 0.7 on SBA-15 and PHTS Samples

adsorbate	SBA-15 n_{ads} (mmol/g)	PHTS-A n_{ads} (mmol/g)	PHTS-B n_{ads} (mmol/g)	$\%n_{ads}{}^a$ (SBA-15)	$\%n_{ads}{}^a$ (PHTS-A)	$\%n_{ads}{}^a$ (PHTS-B)
nitrogen	13.34	11.26	11.66	100	100	100
n-heptane	4.22	4.67		32	41	
n-hexane	7.58	8.69	5.29	57	77	45
c-hexane	6.19	8.54		46	76	
3-methylpentane	7.92	6.71		59	60	
1-hexene	9.69	6.64	6.58	73	59	56
toluene	6.40	4.48	4.10	48	40	35

^{a} $\%n_{ads} = n_{ads}(\text{organic})/n_{ads}(\text{nitrogen}) \times 100$.
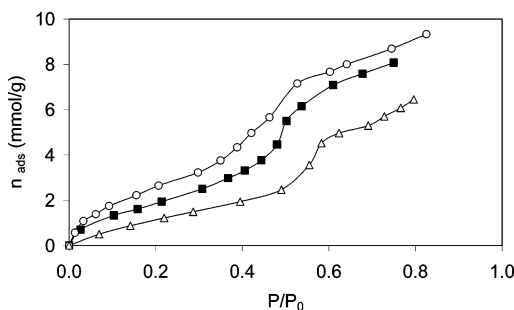
Figure 4. Adsorption isotherms of *n*-hexane on SBA-15 (■), PHTS-A (○), and PHTS-B (△) at room temperature.

Figure 5. Adsorption kinetics of *n*-hexane on SBA-15 (■), PHTS-A (○), and PHTS-B (△) at room temperature.

experiences diffusion limitations. *c*-Hexane is larger than 3-methylpentane, but it still condenses around the same relative pressure on PHTS-A as on SBA-15. In the same way as concluded for the adsorption in the low relative pressure region, the shape of the molecule has to be also considered.

What is striking about the results in Table 3 is that all molecules are adsorbed with a higher efficiency on PHTS-A. Especially *n*-hexane and *c*-hexane show a very high difference of 20% and 30%, respectively, between SBA-15 and PHTS-A. It is also these two adsorbates which show a higher uptake for PHTS-A in the low relative pressure region, which can explain this difference. It can be concluded that the *c*-hexane and *n*-hexane molecules are piled the most efficiently of all molecules in PHTS-A.

Effect of a Different Ratio of Plugged and Open Pores. The effect of a different ratio of plugged and open pores in the PHTS material was investigated by the adsorption of *n*-hexane on PHTS-A and PHTS-B. The main difference between the two samples is the open mesopore volume: 0.16 mL/g for PHTS-A and 0.25 mL/g for PHTS-B (see Table 1). Since the plugged mesopore volume is about the same, the ratio of open to plugged mesopores (V_o/V_{pl}) is 0.55 for PHTS-A and 1 for PHTS-B. Figure 4 shows the adsorption of *n*-hexane on SBA-15, PHTS-A, and PHTS-B. It is striking that the adsorption isotherm of PHTS-A is situated completely above and the one of PHTS-B completely below the isotherm of SBA-15. It seems illogical that more *n*-hexane adsorbs on PHTS-A since PHTS-B has a larger open mesopore volume. Moreover, SBA-15 and PHTS-B have a comparable micropore volume so that an equal uptake of *n*-hexane in the low relative pressure region is expected. The position of the isotherms in Figure 4 can be explained considering that the calculation of the open and plugged mesopore volume is based on N$_2$ sorption. As a consequence it is possible that part of the channels situated behind a plug are not accessible for *n*-hexane as opposed to N$_2$. In this way *n*-hexane cannot access the mesopore volume behind the plugs and the micropore volume of other plugs present behind the plug causing the obstruction. This results in a lower *n*-hexane adsorption in the low as well as the high relative pressure region so that the isotherm of *n*-hexane on PHTS-B is situated
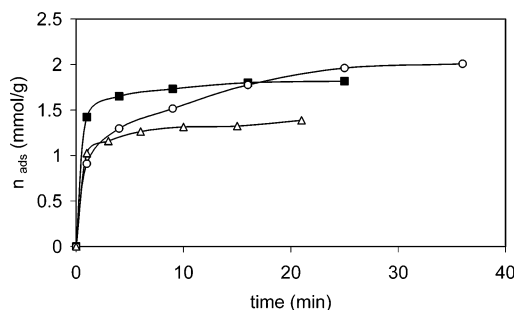
below the ones of SBA-15 and PHTS-A. Since PHTS-B has a higher open mesopore volume but adsorbs less *n*-hexane than PHTS-A, it can be concluded that the plugs of this material are larger than those of PHTS-A. This conclusion is supported by the results of the adsorption kinetics of *n*-hexane on SBA-15, PHTS-A, and PHTS-B (Figure 5). The adsorption−desorption equilibrium of *n*-hexane on SBA-15 and PHTS-B is already reached after 9 min, whereas that on PHTS-A is reached only after 25 min. These data support the previous conclusion as follows. The kinetics on PHTS-A is slower because *n*-hexane can still diffuse through the remaining pore opening next to the plugs. As a result the pore volume behind the plugs is available for adsorption too. On the other hand, the kinetics on PHTS-B is faster than that of PHTS-A because part of the pore volume is blocked for *n*-hexane since the molecule cannot diffuse past the small pore openings next to the plugs. From these data it can be concluded that the adsorption behavior on PHTS is determined by the ratio of open and plugged pores and the size of the plugs, which depend on the synthesis conditions.

Effect of the Polarity of the Adsorbate. Because of the porosity of the plugs, it is possible that they contain a lot of silanol groups rendering PHTS materials more hydrophilic than SBA-15 materials, which in turn can influence the adsorption behavior. To look into this, water adsorption isotherms were recorded on SBA-15, PHTS-A, and PHTS-B. All isotherms in Figure 6 are of type V. PHTS-A has a higher initial and overall water uptake than PHTS-B and SBA-15 so that it can be concluded that PHTS-A is more hydrophilic. This hydrophilicity can be related to the plugs as explained above. As concluded in the previous section, the plugs of PHTS-B are larger than the ones of PHTS-A. Moreover PHTS-B has a lower micropore volume than PHTS-A. This leads to the conclusion that the silica of the PHTS-B plugs is more condensed so that less hydrophilic silanol groups are present leading to a more hydrophobic material.

The effect of the polarity of the adsorbate was investigated through *n*-hexane, 1-hexene, and toluene adsorption on SBA-15, PHTS-A, and PHTS-B. The dipole moments of the adsorbates are shown in Table 2. 1-Hexene
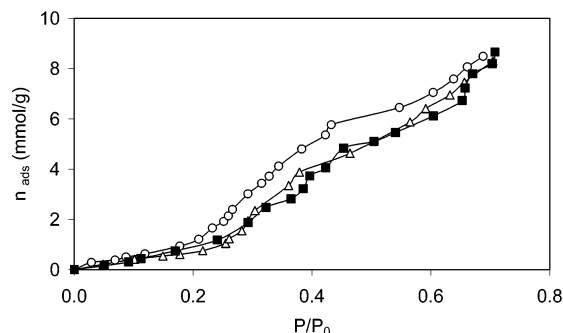
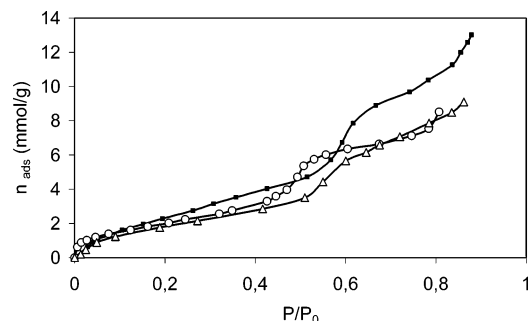**Figure 6.** Adsorption isotherms of water on SBA-15 (■), PHTS-A (○), and PHTS-B (△) at room temperature.

Figure 7. Adsorption isotherms of 1-hexene on SBA-15 (■), PHTS-A (○), and PHTS-B (△) at room temperature.

Figure 8. Adsorption isotherms of 1-hexene (+), n-hexane (×), and toluene (▲) on PHTS-A (a) and PHTS-B (b) at room temperature.

is more polar than toluene because it does not have a delocalized π-system.

In Figure 7 the adsorption isotherms of 1-hexene on these materials are shown. The initial 1-hexene uptake (before $P/P_0 < 0.1$) is higher for PHTS-A than for the other materials. This observation has two explanations. As could be concluded from Figure 6, PHTS-A is more hydrophilic than SBA-15 and PHTS-B so that the polar 1-hexene has a stronger affinity for the PHTS-A surface. From a study[17] of the adsorption of ethene and propene and their corresponding alkanes on SBA-15, it was observed that the olefins showed a higher uptake and a higher isosteric heat of adsorption. The latter suggested that the SBA-15 framework had a higher affinity for olefins, which was ascribed to the presence of framework microporosity. Moreover, higher isosteric heats of adsorption and uptakes were observed with increasing micropore volume.[18] Since PHTS-A has the highest micropore volume of the three materials, it can be concluded that the high initial uptake is also due to the high micropore volume. Furthermore, capillary condensation occurs first on PHTS-A and thereafter on the more hydrophobic materials SBA-15 and PHTS-B. As opposed to the adsorption of n-hexane on these materials, the total volume of adsorbed 1-hexene on PHTS-A is in this case comparable to that on PHTS-B and lower than the one of SBA-15. The above explanations can also elucidate these observations. Because the plugs of PHTS-A are hydrophilic, 1-hexene adsorption will preferentially occur at these sites, leading to a high local adsorption which extends the dimensions of the plug. In this way previously adsorbed 1-hexene molecules can hamper adsorption of following molecules, leading to a lower adsorbed amount of 1-hexene.

The adsorption isotherms of toluene on SBA-15, PHTS-A, and PHTS-B are shown in Figure S4 of the Supporting Information. Toluene has the largest kinetic diameter of the investigated adsorbates (Table 2). Like n-hexane in Figure 4, toluene also shows an overall lower adsorbed amount on PHTS-B, which can be explained in an
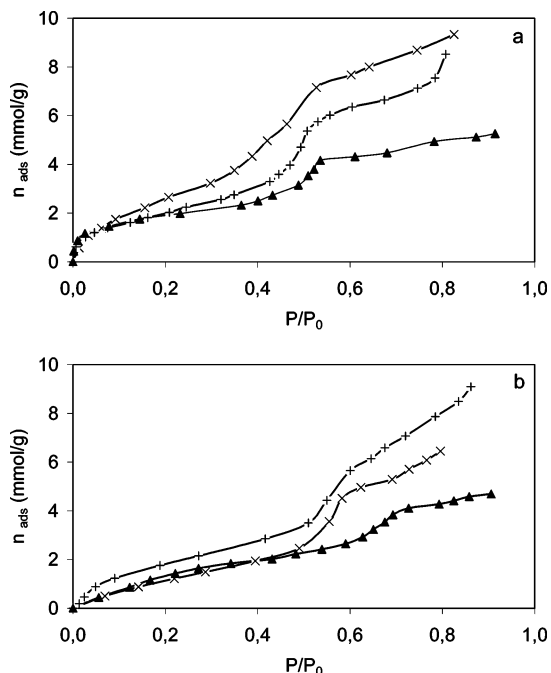
analogous way as for n-hexane. From the previous section, it was concluded that the plugs of PHTS-B are larger than those of PHTS-A. As a consequence, the pore volume behind the plugs of PHTS-B is not available to toluene, which results in a lower toluene adsorption on PHTS-B over the entire relative pressure region.

Figure 8a,b depicts the adsorptions of n-hexane, 1-hexene, and toluene on PHTS-A and PHTS-B, respectively. The results of SBA-15 are shown in Figure S5 of the Supporting Information. Considering the nature of the surface of the materials and the (a)polarity of the adsorbates, a higher adsorbed amount of 1-hexene on PHTS-A and n-hexane on PHTS-B is expected. However, Figure 8a,b records the opposite, which can be explained as follows. In Figure 8a the lower adsorbed amount of 1-hexene opposed to n-hexane can be explained as above: 1-hexene adsorbs on the hydrophilic plugs of PHTS-A and hampers the adsorption of following molecules. Since n-hexane is apolar, it will preferentially adsorb on the pore wall of PHTS-A so that the remaining pore opening at the hydrophilic plugs is not blocked, resulting in an overall higher adsorption. Figure 8b shows the adsorption isotherms of the adsorbates on PHTS-B. As opposed to Figure 8a, there is a distinct difference in adsorption in the low relative pressure region of the isotherms in Figure 8b. As discussed above, part of the pore system of PHTS-B is likely not accessible to n-hexane and larger molecules due to the presence of larger plugs. However, these plugs seem to have less influence on 1-hexene since it has a higher uptake in the low relative pressure region. It could be that because 1-hexene is polar (as opposed to n-hexane) and linear (as opposed to toluene) it can pass the hydrophobic plugs of PHTS-B.

Figures 8a and S5 display the toluene adsorptions on PHTS-A and SBA-15. Although toluene has the largest kinetic diameter, the adsorption in the low relative pressure region is comparable to that of n-hexane and 1-hexene. From this it can be deduced that toluene can still adsorb into the micropores. The total adsorbed amount of toluene however is lower than that of 1-hexene and n-hexane in all cases, which is due to the larger size of

this molecule. Table 3 shows the adsorbed amount of 1-hexene and toluene on the adsorbents. The last three columns express the adsorbed amount of organic to the amount adsorbed of nitrogen in percent. This shows that for 1-hexene and toluene SBA-15 is more efficient than PHTS-A, which in turn is better than PHTS-B. For the alkanes however PHTS-A is more efficient. This demonstrates the large effect of the polarity of the adsorbate (or the nature of the plugs) on the adsorption behavior of hydrocarbons.

Conclusion

The adsorption properties of PHTS were studied and compared to those of SBA-15. The adsorption of n-hexane, c-hexane, n-heptane, 3-methylpentane, 1-hexene, and toluene on SBA-15, PHTS-A, and PHTS-B demonstrated that the presence of the plugs had an effect on the uptake of adsorbate in the low relative pressure region, the position of the capillary condensation step, and the total adsorbed amount of adsorbate. The results showed that n-heptane and 3-methylpentane could not access part of the micropore system of SBA-15 and PHTS-A. A higher adsorption of c-hexane and n-hexane on PHTS-A in the low relative pressure region indicated that this is not the case for these molecules. This does not concur with the kinetic diameters of the adsorbates, which indicates that the shape of the molecule is also an important factor for adsorbing into the SBA-15 and PHTS micropores. PHTS-A proved to be a better adsorbent for alkanes than SBA-15, at which a difference of 20 and 30% for n-hexane and c-hexane between the two adsorbents was demonstrated. From the adsorption of n-hexane on PHTSs with a different ratio of open and plugged pores, it was concluded that the size of the plugs differed, which depends on the synthesis conditions. To investigate the influence of the polarity of the adsorbates, first water isotherms were recorded which proved SBA-15 and PHTS-B to be more hydrophobic than PHTS-A. n-Hexane, 1-hexene, and toluene adsorptions showed higher uptakes for polar adsorbates on more hydrophobic materials and vice versa, which was ascribed to the nature of the plugs. Concluding, the results showed that for an adequate adsorption of these types of hydrocarbons the synthesis conditions of PHTS have to be chosen carefully because these influence the size and nature of the plugs and as a consequence the adsorption behavior. The results also indicate that PHTS materials such as PHTS-A will even perform better for smaller molecules given the fact that the size of these plugs did not hamper c-hexane and n-hexane adsorption and the high micropore volume of the material.

Supporting Information Available: The nitrogen sorption isotherms of SBA-15, PHTS-A, and PHTS-B; the adsorption isotherms of toluene on these materials; and the isotherms of 1-hexene, n-hexane, and toluene on SBA-15. This material is available free of charge via the Internet at http://pubs.acs.org.

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