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Chemical modification of high-quality large-pore M41S materials

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M41S materials with a pore diameter of 80 Å and MCM-41 materials with a pore diameter of 30 Å were grafted with a variety of trimethoxysilanes and chlorosilanes. The obtained hybrid materials were characterised by thermogravimetric analysis, nitrogen adsorption measurements and multi nuclear MAS NMR. A comparison of grafting in the liquid and in the gas phase proved that the former method was more efficient: the amount of grafted material was about 20% higher. Of the 80 Å M41S and the 30 Å MCM-41 material, the former resulted in a higher loading of grafted species and a much larger free pore diameter after grafting. It is, therefore, the better starting material for grafting reactions. By optimising the liquid-phase synthesis the loading of grafted material could be increased by 30% compared to the standard method described in the literature. Furthermore, the degree of condensation of the grafted species was higher with the optimised method, as proven by ^{29}Si MAS NMR.

Introduction

Since bulky molecules have limited access to the internal pore volume of microporous materials such as zeolites, their use as catalysts for the synthesis of fine chemicals is limited. With the discovery of MCM type materials by Mobil researchers, a route was opened to overcome these constraints.[1,2] Due to the significantly larger pore diameter of about 20 to 35 Å, bigger molecules can diffuse inside the pore structure of MCM particles, thereby making the catalytically active sites available for reaction. MCM-41 materials are promising supports in applications requiring large pores because of their well-defined mesoporous structure in combination with a high surface area. The typically attainable pore diameter of about 35 Å, however, is still too small for some applications. Different methods have been published by which materials with an ordered hexagonal pore system and pore diameters up to 50 Å can be generated, whereas materials with larger pore diameters were only obtained with very broad pore size distributions.[1–7] We previously reported the synthesis of M41S materials with a pore diameter of 80 Å. They exhibited a very narrow pore size distribution resembling that of MCM-41, even though the pore system was not hexagonally ordered.[8]

Due to their outstanding porosity the M41S materials are promising for application in catalysis as well as in sorption or separation processes, especially in fine and pharmaceutical chemistry. However, the acidity of aluminium-containing M41S materials is much weaker than that of zeolites due to the amorphous structure of the pore walls. The rather high concentration of surface silanol groups can be used to overcome this disadvantage. By a condensation reaction with these silanol groups functional sites can be introduced, *e.g.*, by the grafting of silanes. Alkoxysilanes or chlorosilanes with a wide variety of organic groups are commercially available. Therefore many potential surface modifications are possible by grafting.

In principle, there are two methods for obtaining M41S hybrid materials, either by direct co-condensation of the grafting agent during the M41S synthesis or by the subsequent grafting of the calcined mesoporous material.[9] The stability of mesoporous silicates is enhanced by the condensation of silanol groups during calcination. Materials prepared by co-condensation cannot be calcined, because the organic moieties would be destroyed. Therefore, the final product lacks stability. In addition, it has been shown that the concentration of the grafted species is much lower for the co-condensation route.[9]

So far, several methods of grafting M41S materials have been published, be it to heterogenise metal organic catalysts, to generate acid sites, or to obtain adsorbents.[9–14] As the grafting procedure introduces additional material inside the pore system the pore diameter is reduced.[9,15] For this reason it is recommended to use large-pore M41S materials rather than MCM-41 as the support for grafted species. Moreover, a larger pore diameter is desired for a number of practical applications where pore diameters of 35 Å, typical for MCM-41, are still too small.

The large-pore M41S materials used for the grafting experiments were produced by pH-adjusted M41S syntheses using short-chain co-surfactants and mesitylene as the swelling agent.[8] In order to generate acid sites within the pore structure these materials were grafted with phenyltrimethoxysilane and subsequently sulfonated with chlorosulfonic acid.[15] These catalysts exhibited high acid loading and strong acidity, as proven by titration and MAS NMR. Since leaching of the active species is effectively inhibited, these materials should be good catalysts for gas phase reactions. Silica catalysts impregnated with benzenesulfonic acid are, for example, good catalysts in the gas phase nitration of benzene.[16] In liquid-phase systems, the benzenesulfonic acid might be less stable due to the reversibility of the sulfonation under certain chemical conditions. Nevertheless, due to the variety of different substitution reactions with the grafted phenyl group these materials offer many other possibilities for further derivatisation besides sulfonation.

In continuation of the work presented previously[15] we describe here different approaches to phenyl-grafting in the gas and liquid phase. The grafting procedure was optimised with respect to a high loading of the grafted species and an enhanced quality of the final hybrid material. The properties of grafted 80 Å M41S were compared to those of MCM-41.

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In order to overcome the limitations associated with aromatic sulfonic acids the grafting of (3-iodopropyl)trimethoxysilane was also investigated. The iodopropyl-grafted M41S materials can be used as starting reagents for the formation of grafted alkanesulfonic acids by nucleophilic substitution of the iodine with sulfite ions.[17,18] Alkanesulfonic acid is much more stable than arenesulfonic acid in the liquid phase.

Experimental

Syntheses

The pure silica large-pore M41S material was synthesised as reported previously.[8] This highly porous solid with a pore diameter of 80 Å was used as the support for the subsequent grafting experiments. Phenyl-grafted M41S was synthesised either in the gas phase with methyl(phenyl)dichlorosilane or in liquid phase with phenyltrimethoxysilane as grafting reagents. The former was performed according to a method reported by Sindorf and Maciel,[19,20] either at ambient pressure under nitrogen atmosphere or in a closed pre-evacuated system. In both cases the support material was dried prior to the synthesis by heating at 200 °C for 3 h. The grafting under nitrogen atmosphere was carried out by refluxing the chlorosilane in a flow of nitrogen. The dried support was exposed to the gas mixture in a separate part of the apparatus. After the system was equilibrated the nitrogen flow was stopped and the part of the apparatus containing the M41S material was heated to 110 °C. The heating was continued for 18 h.

The second gas phase grafting procedure was performed in a static closed glass system that was evacuated prior to reaction. In this system the M41S and the silylating agent were placed in separate containers. The grafting agent was vaporised by heating the whole system to 110 °C for 18 h.

The liquid phase grafting was performed according to the procedure described by Feng *et al.*[14] Prior to synthesis, the M41S material was refluxed in water for 3 h in order to generate a maximum number of silanol groups on the silica surface, assumed by Feng *et al.* to be 5×10^{18} SiOH per m^2. The water-treated material was collected by filtration. Some of the remaining water ($1.3\ ml\ g^{-1}$ of a total of $1.8\ ml\ g^{-1}$) was subsequently removed by azeotropic distillation in benzene. After cooling to ambient temperature a fourfold excess of the grafting reagent was added to the slurry. This mixture was stirred for 14 h at ambient temperature and subsequently refluxed for 4 h. The final product was collected by filtration and washed with propan-2-ol in order to remove the excess grafting reagent.

To optimise the synthesis procedure of Feng *et al.* we investigated in detail the influence of the three synthesis steps. The duration of pre-treatment with water was systematically varied from 0 to 180 min, the amount of excess water removed by azeotropic distillation was varied between zero and $1.8\ ml\ g^{-1}$ (the maximum) and the time of refluxing the reaction mixture with the grafting reagent was varied from 0 to 4 h. The pore characteristics (pore volume and size), the amount of reactive silanol groups and the loading of grafted species were compared as a function of these three parameters.

When comparing different figures and tables, small differences in the pore characteristics of the parent materials can be found. This is due to the reproducibility of the synthesis. The data in each figure/table were obtained from a different batch of parent material.

Characterisation

Nitrogen adsorption of the calcined samples was measured at −196 °C with an ASAP 2010 Micromeritics apparatus. Prior to the measurements the calcined samples were degassed at 400 °C for 4 h at a pressure of less than 1.4 Pa and the grafted samples were degassed at 120 °C overnight. The surface area was determined from the nitrogen adsorption isotherm by the BET method,[21] the pore size distribution from the desorption branch by the BJH method[22] and the pore volume by the *t*-plot method.[23] As the adsorption behaviour of nitrogen depends on the surface characteristics and on the pore diameter,[24] which both change during the grafting, the results of nitrogen adsorption have to be interpreted with much caution. It must also be considered that the values of the surface area and the pore volume are referenced to the sample weight, which increases due to grafting. This can be corrected for, but it introduces an additional error. Nevertheless, the BJH method is usually applied as the standard method for the pore size determination and is well suited to analyse trends in similar samples. Thus, we also used this method to compare the pore size characteristics and texture of our MCM-41 and M41S samples.

The loading of the grafted materials was mainly determined by thermogravimetric analysis (TGA). TGA was performed with a Mettler Toledo TGA/SDTA 851^e thermal balance at a heating rate of $5\ °C\ min^{-1}$ up to 800 °C in a flow of air.

Solid state MAS NMR spectra were recorded using a Bruker AMX 400 spectrometer at 9.4 T, which corresponds to 400.13 MHz for ^1H, 79.49 MHz for ^{29}Si and 100.61 MHz for ^{13}C. For the ^1H NMR measurements the samples were degassed at 120 °C for 3 h at reduced pressure and sealed in zirconia rotors.[25] Signals in the ^{29}Si NMR spectra are referred to by the symbols Q^n and T^n. Q^n stands for $Si(OSi)_n(OH)_{4-n}$ and T^n for $SiR(OSi)_n(OH)_{3-n}$.

Results and discussion

Comparison of grafting in the gas and liquid phases

Table 1 compiles the results of the grafting of phenyl species in the liquid and gas phase for MCM-41 and M41S by different methods. Of the two methods of gas phase grafting, the procedure under vacuum was more successful than grafting under nitrogen atmosphere. The phenyl loading was twice as high. However, because of the lower concentration of silanol groups, the gas-phase grafting generally led to lower loadings than liquid-phase grafting. The porous solids must be dried before grafting in the gas phase, leading to a condensation of the silanol groups. In the liquid phase reaction, on the other hand, pre-treatment with water enables the generation of additional silanol groups on the surface. Therefore, further grafting experiments were performed with the liquid phase system.

In principle, a closely packed layer of the grafted species is desired since the grafted molecules cover the silicate surface and, thus, hinder its destruction by hydrolysis.[14,26] The stability of these hybrid materials will be further enhanced when the grafted species are linked together by siloxane bridges, for which a high density of grafted species is also a prerequisite. The concentration of the silanol groups clearly plays a key role in this respect. Therefore, the changes in Si–O–Si connectivity and the increase in the number of silanol groups during the water-treatment were monitored by ^{29}Si MAS NMR (Fig. 1). The broad signal between 100 and 110 ppm, assigned to an overlap of the two signals of Q^3 (about 100 ppm) and Q^4 (about 110 ppm) silicon atoms, became better resolved. The Q^3 signal increased and an additional signal at 91 ppm assigned to Q^2 silicon appeared. The higher resolution of these signals is caused by the partial breaking of siloxane bridges and, thus, the formation of a less strained structure, in terms of the O–Si–O bond angles. The additional Q^3 and Q^2 species confirm these findings. The influence of the water pre-treatment on pore diameter, pore volume and surface area of the phenyl-grafted materials was more pronounced for the large-pore M41S

Table 1 Data from nitrogen adsorption and TGA for the two parent materials, phenyl-grafted MCM-41 (30 Å) and M41S (80 Å)

Sample[a]	Surface area (BET)/m^2 g^{-1}	Pore diam. (BJH)/Å	Mesopore vol. (t-plot)/cm^3 g^{-1}	Δm (TGA) (%)	Amount of grafted species (TGA)/mmol g^{-1b}	
MCM-41c	1103	27	0.87	—	—	—
MCM-41c-ph	970	22	0.53	18	2.6	3.9
MCM-41w-ph	955	21	0.49	20	2.8	4.5
MCM-41gN-ph	855	21	0.49	5	0.7	0.8
M41Sc	1186	78	2.71	—	—	—
M41Sc-ph	956	70	1.81	20	2.8	4.5
M41Sw-ph	726	60	0.93	28	4.1	9.2
M41SgN-ph	1162	76	2.72	13	1.9	2.5
M41SgV-ph	707	67	1.50	25	3.6	6.8

[a] c = calcined parent material; c-ph = phenyl grafted without water pre-treatment (liquid phase); w-ph = phenyl grafted with water pre-treatment (liquid phase); gN-ph = phenyl-grafted under nitrogen (gas phase); gV-ph = phenyl-grafted in vacuum (gas phase). [b] In the left column the data are expressed in mmol g^{-1} of the final material, in the right column in mmol g^{-1} of the MCM41/M41S support, *i.e.*, corrected for the weight gain during grafting.

material (Table 1). The same trend was observed in the TGA results. They showed a generally greater weight loss for the samples pre-treated with water, indicating a higher loading of phenyl groups. The lower phenyl loading of the 30 Å material is due to steric constraints inside the pores. The smaller pore diameter of MCM-41 causes a greater curvature of the surface and, thus, the steric interaction of the grafted species is stronger. In MCM-41 materials the additionally generated silanol groups can only partially react with the grafting agent, indicating that the silanols present in the parent material already correspond to almost the maximum loading attainable. On the other hand, the less curved pore surface of 80 Å-M41S allows a closer arrangement of the phenyl groups and the loading is mainly limited by the silanol concentration. These results demonstrate the clear advantage of the large-pore M41S material.

Optimisation of the liquid phase grafting procedure

The water pre-treatment in the grafting procedure described by Feng *et al.*[14] serves to increase the number of reactive silanol groups. Excess water has to be removed prior to grafting, however, because it might catalyse internal condensation reactions of the grafting agent. It is worth taking a closer look at these pre-treatment steps as well as the actual grafting reaction itself, because an optimisation of the synthesis could lead to a more dense and interconnected layer of grafted material. Therefore, the parameters of the three synthesis steps were systematically varied, as described in the Experimental section. The investigations were carried out with the cheaper grafting reagents methyl- and propyl-trimethoxysilane.

The major importance of the treatment with water, the first post-synthesis step, has already been described in the previous section. Longer pre-treatment with water could lead to a higher concentration of reactive silanol groups but also to a destruction of the pore system since M41S materials are unstable against hydrolysis. The pore characteristics of M41S after treatment with water for 0 to 180 min are listed in Table 2. Only a small reduction in the pore volume and surface area was observed after 30 min. Longer treatment did not significantly change the properties. This suggests that the weaker siloxane bridges are hydrolysed first. They are certainly those with stressed bond angles. Following this relaxation of the silicate system the hydrolysis stops. This assumption is proven by a higher resolution of the ^{29}Si MAS NMR after water treatment (Fig. 1).

The concentration of the reactive silanol groups as a function of the duration of water pre-treatment was evaluated by the yield of grafted material after reaction with methyltrimethoxysilane (Table 3). The treated material showed a significantly higher loading of methyl species. Treating with water for more than 30 min did not bring about remarkable changes in the yield of grafted species. The ^{29}Si MAS NMR spectra of the different grafted species show the same trend (Fig. 2). After a water-treatment of only 30 min, a change in the intensities of the signals of the grafted silicon atoms (T^n) was already

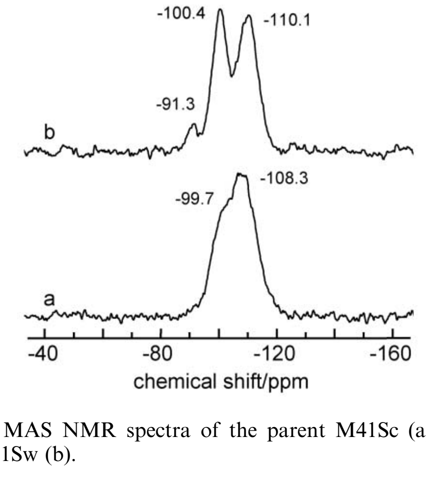

Fig. 1 ^{29}Si MAS NMR spectra of the parent M41Sc (a) and water treated M41Sw (b).

Table 2 Data from nitrogen adsorption of the parent M41Sc and samples after different durations of treatment with water[a]

Water treatment/min	Surface area (BET)/m^2 g^{-1}	Mesopore vol. (t-plot)/cm^3 g^{-1}	Pore diam. (BJH)/Å
Parent M41Sc	1155	2.72	80
30	1056	2.52	79
60	1036	2.45	79
120	1030	2.44	78
180	1040	2.41	78

[a] Samples were dried by azeotropic distillation, filtered and dried under vacuum at 50 °C over night.

Table 3 Data from nitrogen adsorption and TGA of the parent M41Sc and methyl-grafted[a] samples after different durations of treatment with water

Water treatment/min	Surface area (BET)/m^2 g^{-1}	Pore diam. (BJH)/Å	Mesopore vol. (t-plot)/cm^3 g^{-1}	Δm (TGA) (%)
Parent M41Sc	1150	79	2.77	—
0	711	66	1.50	7.7
30	575	66	1.38	8.5
60	538	63	1.25	9.5
120	545	64	1.27	8.8
180	516	62	1.17	9.5

[a] All grafting steps except of the water treatment according to Feng *et al.*[14]

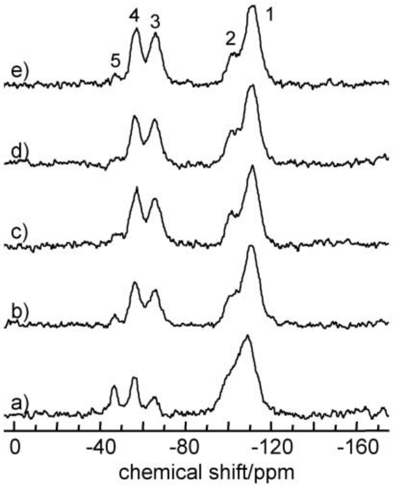

Fig. 2 ^{29}Si MAS NMR spectra of propyl-grafted M41S after 0 min (a), 30 min (b), 60 min (c), 120 min (d) and 180 min (e) of treatment with water. Peak positions: −111 ppm (1), −102 ppm (2), −66 ppm (3), −57 ppm (4), −48 ppm (5).

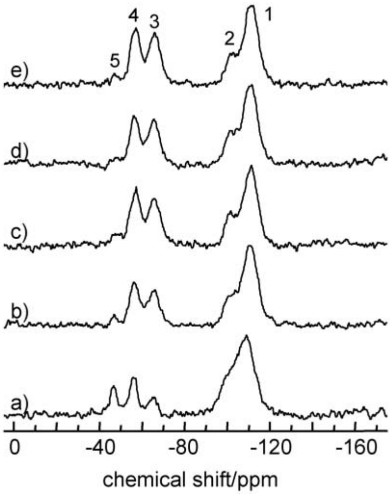

Fig. 3 ^{29}Si MAS NMR spectra of propyl-grafted M41S after different azeotropic distillations: 0 ml (a), 0.7 ml (b), 1.1 ml (c) and 1.5 ml (d) of water removed. Peak positions: −111 ppm (1), −101 ppm (2), −92 ppm (3), −66 ppm (4), −57 ppm (5), −48 ppm (6).

observed. The intensity of the T^1 species is much lower than that of the T^2 and T^3 species, indicating a higher degree of condensation of the grafted species. Surprisingly, the signal at about 100 ppm, which is usually assigned to Q^3 species, is more pronounced for the water-treated samples, even though the degree of condensation was expected to be higher. The increased intensity of this signal is explained by the so-called “triangle Q^4’ species ($Q^4_\triangle$), which are Q^4 silicon atoms that are part of a triangle of one grafted silicon atom connected with two neighbouring surface silicon atoms.[27] The differences between the spectra of samples with different durations of treatment with water are only small, which is in good agreement with the other data. From this we conclude that a 30 min pre-treatment is sufficient to increase the concentration of reactive silanol groups. Further pre-treatment does not bring about significant improvement.

A similar optimisation was carried out for the second pre-treatment step, where excess water is removed by azeotropic distillation. The excess water could lead to unwanted internal condensation reactions of the grafting agent. Removing too much water, however, could lead to a re-condensation of the created silanol groups. The optimum amount of water that should be removed was suggested to be 1.4 ml per g M41S material.[14] The TGA and nitrogen adsorption data of propyl-grafted samples from which different amounts of water had been removed by azeotropic distillation are presented in Table 4. The more water had been removed by azeotropic distillation, the smaller was the weight loss in TGA. At the same time the surface area, and also the pore volume and the pore diameter increased. The same effect was observed in the ^{29}Si MAS NMR spectra (Fig. 3). The distribution of different T^n species shifted towards the less condensed T^1 species when more water was removed. Furthermore, the intensity of the signals of the grafted silicon atoms decreased as more water was removed. These results clearly show that, in the case of our 80 Å M41S, the number of grafted species decreased even when small amounts of water were removed. The re-condensation of silanol groups during distillation leads to a lower concentration of anchoring sites for the grafting agent and, thus, to a lower loading.

In the final step of the grafting procedure we examined the influence of the refluxing time, which was varied from 0 to 4 h. The number of grafted propyl groups increased within the first hour but decreased again with refluxing time, as can be seen from the nitrogen adsorption and the TGA data (Table 5). These results correspond to those of the ^{29}Si MAS NMR spectra (Fig. 4). The optimum ratio of the different T^n silicon atoms was obtained after one hour of refluxing but shifted towards the less condensed species with longer refluxing time. We conclude that short refluxing (1 h) completes the condensation reaction. Prolonged refluxing, however, can reverse the reaction and reduce the number of grafted species under the present reaction conditions.

Grafting of iodopropyl groups

The anchoring of iodoalkyl groups to M41S was carried out as a first step towards the preparation of immobilised aliphatic sulfonic acids. Table 6 gives the comparison of iodopropyl-grafted M41S, which was synthesised according to the literature or to our optimised procedure. The number of grafted species increased considerably in our procedure, which can be mainly attributed to the increased number of silanol groups due to the changes in the azeotropic distillation step. The nitrogen adsorption data show that the pore structure was not destroyed. Changes in the surface area and the pore volume

Table 4 Data from nitrogen adsorption and TGA of the parent M41Sc and propyl-grafted[a] samples after different azeotropic distillations

Removed water/ml g^{-1}	Surface area (BET)/m^2 g^{-1}	Pore diam. (BJH)/Å	Mesopore vol. (*t*-plot)/cm^3 g^{-1}	Δ*m* (TGA) (%)
Parent M41Sc	1115	77	2.36	—
0	527	57	1.02	18
0.7	651	63	1.37	16
1.1	701	64	1.48	15
1.5	807	68	1.72	11

[a] all grafting steps except of the azeotropic distillation according to Feng *et al.*[14]

Table 5 Data from nitrogen adsorption and TGA of parent and propyl-grafted[a] M41S after different durations of reflux

Time of reflux/h	Surface area (BET)/m^2 g^{-1}	Pore diam. (BJH)/Å	Mesopore vol. (*t*-plot)/cm^3 g^{-1}	Δ*m* (TGA) (%)
Parent M41Sc	1128	76	2.32	—
0	662	62	1.34	14
1	599	61	1.22	17
2	646	60	1.30	15
4	664	60	1.31	14

[a] All grafting steps except of the reflux durations according to Feng *et al.*[14]

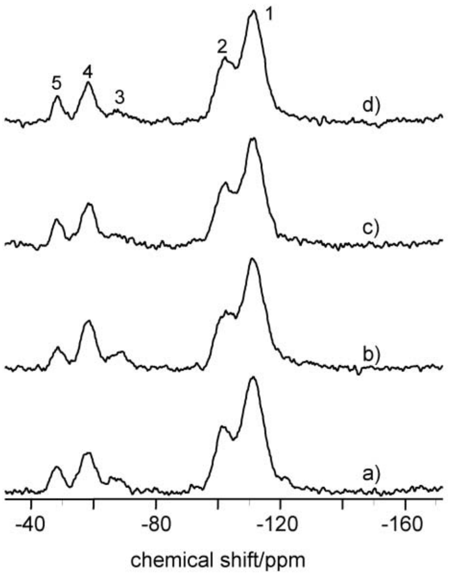

Fig. 4 ^{29}Si MAS NMR spectra of propyl-grafted M41S from syntheses with 0 h (a), 1 h (b), 2 h h (c) and 4 h (d) reflux. Peak positions: −111 ppm (1), −102 ppm (2), −68 ppm (3), −58 ppm (4), −49 ppm (5).

are attributed to the reduction in pore size caused by grafting a layer of iodoalkyl groups. As mentioned before, these results of nitrogen adsorption have to be interpreted cautiously, since the nitrogen adsorption is related to the surface characteristics. Therefore, transmission electron microscopy (TEM) images were also used to check the integrity of the pore structure. The TEM images of the grafted M41S samples (not shown) resemble those of the parent materials.[8] Due to the severe conditions of TEM, the organic material cannot be observed, but the M41S structure was clearly intact. Furthermore, no silica debris was observed inside the pores, indicating that no additional silicate species, besides the grafted ones, remained in the final samples after synthesis.

Due to the large size of the iodine atom, it may be necessary to regulate the concentration of functional groups in M41S by co-grafting iodopropyl and propyl groups to enable better access during S_N2 substitutions. Controlling the iodopropyl concentration is, however, only possible if it is known how the surface composition of iodopropyl/propyl corresponds to that in the solution. In order to clarify this point, the grafting of propyl-, iodopropyl-trimethoxysilane and a 1 : 1 mixture of both was performed according to the procedure of Feng *et al.*[14] Table 7 and Fig. 5 compile the results of the characterisation of the final materials by ^{1}H and ^{29}Si MAS NMR and TGA. Quantification of the ^{1}H MAS NMR spectra showed that, within the uncertainties of the peak fitting, the ratio of the grafted species resembled that of the initial grafting mixture. TGA results support that conclusion. Furthermore, the total number of grafted molecules was higher with the propyl groups. The steric repulsion of the larger iodine seems to prevent a higher loading. Nitrogen adsorption data (Table 8) prove the structural integrity of all three samples.

Conclusions

Surface modification of MCM-41/M41S can be performed either by gas-phase or liquid-phase reaction. An inherent advantage of the liquid phase procedure is the possibility of increasing the silanol concentration of the sample prior to grafting by a treatment with water. Thus, the product contains a larger amount of functional groups.

Since the pore diameter shrinks due to the formation of a layer of grafted species, it is recommended that the pore size of the parent material is larger than 30 Å. Moreover, the grafting reaction is hindered in the smaller pores by steric interaction, because the pore surface is more curved than in large-pore materials.

The silanol concentration is the most important parameter in the grafting reaction. It can be maximised by a careful optimisation of the individual synthesis steps. Thus, we obtained a simplified preparation method for grafted M41S materials with a higher loading and a higher degree of condensation. Even the grafting of iodopropyl groups, which are sterically more demanding than propyl groups, yielded materials with 10 mmol g^{-1} iodopropyl by the optimised synthesis.

The post synthesis grafting of M41S materials is a simple method of obtaining highly porous solid materials with a wide variety of surface characteristics that can be tailored for many special applications. Due to their outstanding characteristics, *i.e.* pore volume, pore diameter, and narrow pore size distribution, the grafted large-pore M41S materials, which exhibited significantly higher loadings, are especially promising not only for use as catalysts but also as adsorbents, ion exchangers, and as chromatographic gels.

Table 6 Data from nitrogen adsorption and TGA iodopropyl-grafted M41S synthesised according to the literature[14] and our optimised procedure

Synthesis	Surface area[a] (BET)/m^2 g^{-1}	Pore diam. (BJH)/Å	Mesopore vol.[a] (*t*-plot)/cm^3 g^{-1}	Δm (TGA) (%)	Amount of grafted species (TGA)/mmol g^{-1b}	
Ref. 14	410 (935)	63	0.86 (1.96)	41	2.5	5.7
This work	211 (674)	49	0.40 (1.28)	50	3.1	9.9

[a]The values in parentheses are referenced to the initial weight of the M41S material, *i.e.*, corrected for the weight gain during grafting. [b]In the left column the data were expressed in mmol g^{-1} of the final material, in the right column in mmol g^{-1} of the M41S support, *i.e.*, corrected for the weight gain during grafting.

Table 7 Quantification of the ^{1}H MAS NMR spectra and TGA data from iodopropyl and propyl grafted M41S[a]

	^{1}H MAS NMR[b]				
	C_3H_7/mmol g^{-1}	I–C_3H_6/mmol g^{-1}	Δm (TGA) (%)	Amount of grafted species (TGA)/mmol g^{-1c}	
I–C_3H_6	—	1.9	41	2.5	5.7
I–C_3H_6/C_3H_7	1.3	1.6	30	3.3	6.6
C_3H_7	4.1	—	18	5.1	10.0

[a]All grafting steps according to Feng *et al.*[14] [b]Referenced to the sample weight. [c]In the left column the data are expressed in mmol g^{-1} of the final material, in the right column in mmol g^{-1} of the M41S support, *i.e.*, corrected for the weight gain during grafting.

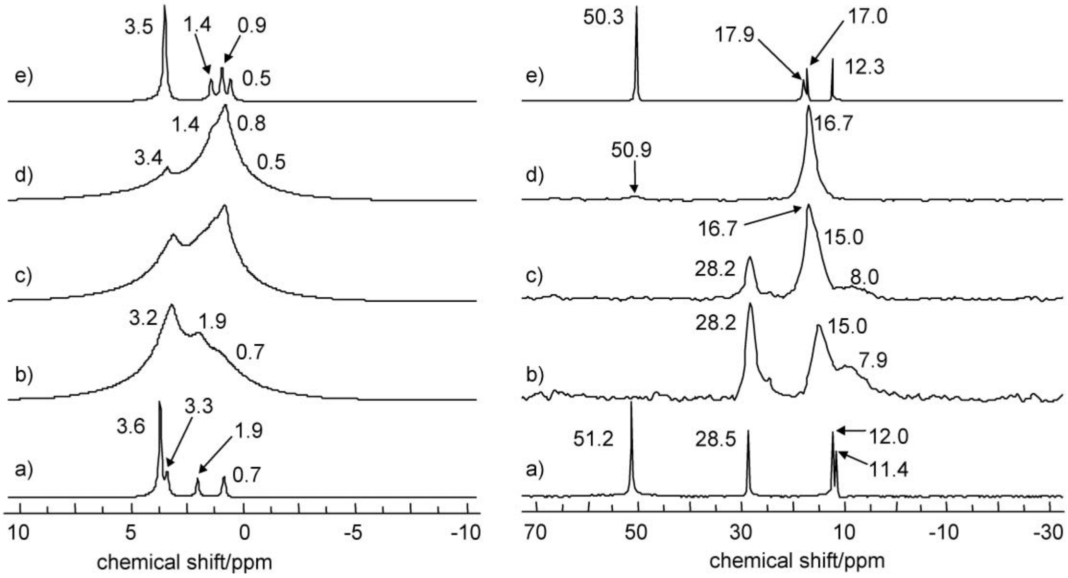

Fig. 5 ^{1}H (left) and ^{13}C MAS NMR spectra (right) of (3-iodopropyl)trimethoxysilane (a), iodopropyl (b), iodopropyl/propyl (c), and propyl grafted M41S (d), and propyltrimethoxysilane (e).

Table 8 Data from nitrogen adsorption of the parent (M41Sc), iodopropyl and propyl grafted samples[a]

	Surface area (BET)/m^2 g^{-1}	Mesopore vol. (t-plot)/cm^3 g^{-1}	Pore diam. (BJH)/Å
M41Sc	1163	2.86	86
I–C_3H_6	410	0.86	63
I–C_3H_6/C_3H_7	511	1.07	64
C_3H_7	492	1.09	61

[a] All grafting steps according to Feng *et al.*[14]

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