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Metal−Organic Modification of Periodic Mesoporous Silica: Multiply Bonded Systems

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The use of metal−organic compounds for the organic modification of mesoporous silica such as MCM-41 leads to a fast, efficient, and economic access to inorganic−organic hybrid materials. Using this method, MCM-41 was modified with short-chain alkenes such as allyl and vinyl groups, as well as styrene and different acetylenic molecules. The resulting modified mesoporous materials were characterized with respect to their structural integrity, surface area, and pore volume and the nature and concentration of the grafted species. These grafted periodic mesoporous inorganic−organic hybrid systems offer the potential for a wide range of further modifications aimed at applications in catalysis, sensing, or chemisorption.

Introduction

The functionalization of mesoporous molecular sieves with organic molecules is motivated by a broad variety of potential applications including sensor technology, catalysis, synthesis of nanoparticles, and chemisorption.[1−4] To achieve these aims, the different functional groups can be introduced either by co-condensation or by postsynthesis grafting.[5,6] The second method is commonly used to introduce groups that are not stable under the strong basic or acidic aqueous conditions used for the synthesis of the mesoporous host materials.[7,8] For example, epoxides and nitriles belong to this group.[9,10] To avoid these stability issues, it is attractive to introduce masked functionalities into the porous silica structure by postsynthesis grafting.[11] Among these groups are olefinic and acetylenic compounds. The implementation of multiply bonded systems into the periodic mesostructure offers the advantage of a wide variety of possible subsequent functionalizations. The multiply bonded moieties can, in principle, be modified by many reactions including electrophilic additions, palladium-catalyzed cross-coupling reactions, or cyclo-additions.[12−14] Figure 1 gives an overview of some of the possibilities for the modification of multibonded systems. In addition to the reactions mentioned above, there are radical additions, the Glaser coupling, boron- or mercury-induced reactions, and others (Figure 1).[15−18]

By postsynthesis grafting of MCM-41 with disilazane agents, Anwander et al. introduced vinyl groups into the mesopores and further modified them by hydroboration.[19] In addition, vinyl groups anchored to mesoporous silica were epoxidized.[20] Allyl groups were introduced into mesoporous silica using both co-condensation and postsynthesis grafting in MCM-41 and analogous materials.[21] To the best of our knowledge, these materials were not further modified. Little is known about the introduction of carbon−carbon triple bonds into mesoporous structures, with one exception presented by C. J. Brinker et al.[22] Various publications regarding triple-bond systems in mesoporous silica are focused on the catalytic polymerization of triply bonded monomers by metal particles supported on mesoporous silica hosts.[23,24]

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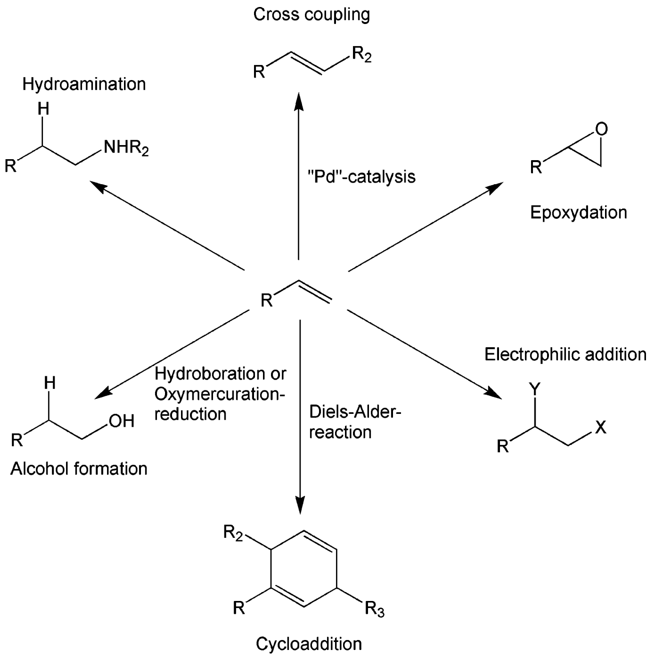

Figure 1. Overview on possible subsequent modification reactions of multiply bonded systems.

The aim of this study is to offer access to different types of multibonded systems inside the pores of MCM-41 by use of fast and efficient metal−organic reactions. Emphasis is placed on the characterization of the successfully incorporated organic groups, as the metalorganic modification of mesoporous silica with representative organic lithium compounds and Grignard reagents has already been studied in detail with respect to the influence of factors such as synthesis time, temperature, and reagent concentrations on the structural integrity, loading, and porosity of the resulting hybrid materials, as well as fundamental issues such as the bonding to the silica framework.[25] On the basis of these results, optimized synthesis conditions were found that we have applied for the functionalization of MCM-type materials with multibonded systems. Because metal−organic reagents for various multiply bonded systems are either commercially available or easily synthesized, this route is advantageous in comparison to classical approaches such as grafting or co-condensation. In the latter cases, trialkoxy- or chlorosilanes of the corresponding systems are needed, which are typically either not commercially available, very expensive, or require substantial synthetic efforts for their generation. Furthermore, it is advantageous that the modification can be performed at room temperature and below, allowing the use of thermally unstable moieties, i.e., biologically relevant molecules, thus further expanding the range of potential groups for surface functionalization of mesoporous silica materials.

The functional groups presented here for the modification of mesoporous silica include vinyl and allyl groups, acetylene groups such as trimethylsilylacetylene and phenylacetylene, and styrene. These molecules were grafted to the surface of the inner pore walls of MCM-41 by use of metalorganic reagents, followed by extensive characterization of the resulting solids.

Experimental Section

Materials. The Grignard compounds vinyl- and allylmagnesium bromide as well as dry THF, trimethylsilylacetylene, phenylacetylene, and 4-bromostyrene were purchased from Sigma Aldrich.

Procedure for the Synthesis of MCM-41. The starting material was synthesized according to a published procedure.[26] For this purpose, 2.40 g (6.59 mmol) of hexadecyltrimethyl-ammonium bromide (CTAB) was dissolved in 120 mL (6.67 mol) of water under stirring (200 rpm for 1 h). Aqueous ammonia solution (9.85 mL, 0.13 mol, 25 wt %) was added to the resulting suspension, and the whole mixture was stirred for additional 5 min (200 rpm). After 10 mL (45.1 mmol) of tetraethylorthosilicate (TEOS) was added, the resulting suspension was stirred for 16 h at 200 rpm at room temperature. The suspension was filtered and washed two times with 50 mL of water and then 50 mL of methanol. The raw material was dried at 90 °C for 16 h in air. The predried solid was calcined in air using a ramping profile. The heating rate was 1 °C min^{-1} up to a temperature of 550 °C. This temperature was kept for 5 h. MCM-41 (2.5 g) was obtained as a colorless solid powder (93% yield related to Si in TEOS).

Synthesis Procedure for the Modification of MCM-41 with Metal−Organic Reagents. MCM-41 (0.25 g) was dried for 15 h at 150 °C under a vacuum. The dried material was cooled to room temperature and suspended in 5 mL of dry THF under a nitrogen atmosphere. The specific metal−organic compound (1.25 mmol; see below) was added dropwise to the stirred suspension. The resulting suspension was stirred for 4 h at room temperature, hydrolyzed by ethanol, and filtered. The remaining powder was washed with 100 mL of water and 100 mL of methanol. The resulting colorless powder was dried at 60 °C in air overnight followed by Soxhlet extraction using methylene chloride.

Synthesis Procedure for the Metal−Organic Acetylene Compounds. The hydrogen metal exchange of the acetylenes took place by deprotonation of the acidic sp carbons of the acetylene derivatives.[27] For this purpose, 1.25 mmol of the respective acetylene derivative was stored in a Schlenk flask under a dry nitrogen atmosphere in 2 mL of THF. The solution was cooled to 0 °C by an ice bath followed by addition of 1 equiv of ethylmagnesium bromide. The respective solutions were stirred for 30 min at room temperature and used directly for the general synthesis procedure for the organic modification mentioned above.

Procedure for the Preparation of 4-Lithium-vinylbenzene. 4-Bromostyrene (1.25 mmol, 227.5 mg) was dissolved in 2 mL of THF in a Schlenk tube under a dry nitrogen atmosphere. The solution was stirred for 15 min, cooled to −78 °C, and stirred again for 15 min at the same temperature. *n*-Butyllithium (1.25 mmol) was added dropwise while the temperature of the reaction mixture was kept constant. The resulting solution was stirred for 15 min at −78 °C and afterward used directly for the organic modification of MCM-41 as mentioned above.

Characterization. Nitrogen sorption measurements were performed on a Quantachrome Instruments NOVA 4000e at a temperature of 77 K. The specific surface area was determined by BET evaluation at relative pressures below 0.3. Pore diameters were obtained using a BJH model (it is believed that the BJH model results in pore diameters that are about 1 nm smaller than the real diameters). Powder XRD patterns were obtained with a Scintag XDS 2000 diffractometer using the Cu−K$_\alpha$ line ($\lambda = 0.15405$ nm). ^{29}Si MAS NMR spectra were recorded on a Bruker DSX Avance

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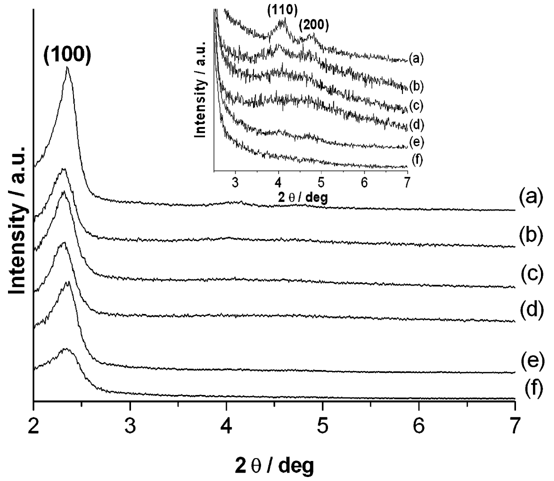
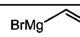
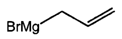
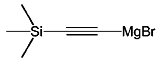
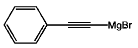
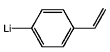


Figure 2. XRD patterns of (a) unmodified MCM-41 and samples (b) VI.MCM, (c) ALY.MCM, (d) TMSAC.MCM, (e) PHAC.MCM, and (f) STYR.MCM. The inset shows a magnification of the region between 3 and 7° 2*θ* for all samples. The patterns are offset to each other.

Table 1. Metal−organic Compounds Used for the Modification of MCM-41

Entry	Structure	Solvent	Sample name
1		Diethylether	VI.MCM
2		THF	ALY.MCM
3		THF	TMSAC.MCM
4		THF	PHAC.MCM
5		THF	STYR.MCM

500 FT-NMR using cross polarization. Transmission electron microscopy (TEM) was performed on a JEOL JEM 2010 microscope at 200 kV. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 440 C instrument by heating a 10 mg sample at a heating rate of 10 °C min^{-1} in a stream of synthetic air (25 mL min^{-1}).

Results and Discussion

In a related article, we report optimized reaction conditions for the organic modification of mesoporous molecular sieves by use of selected metalorganic reagents and the influence of this method on the pore structure and surface texture.[25] On the basis of these results, we present the introduction of organic multiply bonded groups using the metalorganic method (Table 1). Most conversions presented in this paper were carried out at room temperature for 4 h, although in some cases, the reaction was performed at different temperatures (−78 and 68 °C) for comparison purposes. X-ray diffraction data show that the structural integrity was mostly preserved during the metal−organic functionalization reaction (Figure 2). The (100) main reflection is present for all samples; however, the intensity is lowered in comparison to untreated MCM-41 material because of the loss of mass contrast by coating of the mesopore walls with organic material. Magnification at higher diffraction angles shows that all samples with exception of STYR.MCM retain their (110) and (200) reflections. Although in some cases these peaks appear to be slightly broadened, their presence indicates only a minor loss in long-range order. These results were confirmed by TEM analysis, showing the parallel alignment of the pores in sample VI.MCM, as expected for the typical structure of hexagonal MCM-41 material (Figure 3). Analysis of the sorption measurements shows the typical Type IV isotherm for all organically modified solids (Figure 4). The relative pressure at which pore filling occurs in the organically modified samples is shifted to lower values in comparison to the parent material MCM-41. This is caused by the reduction of the pore diameter because of the organic modification. This effect can be quantified via investigation of the pore size distribution curves calculated from the isotherm data (Figure 5). It should be noted that the small peak at about 30−40 Å in the pore size distribution curves is an artifact due to the presence of narrow hysteresis loops, which close at the lower limit of the loop closure and do not correspond to real mesopores in the sample. The reduced pore radii combined with both the reduction of the specific surface area and the specific pore volumes confirm the organic modification of the inner surface of the channels. The respective surface areas, pore volumes, and pore diameters obtained from nitrogen sorption for all samples are summarized in Table 2.

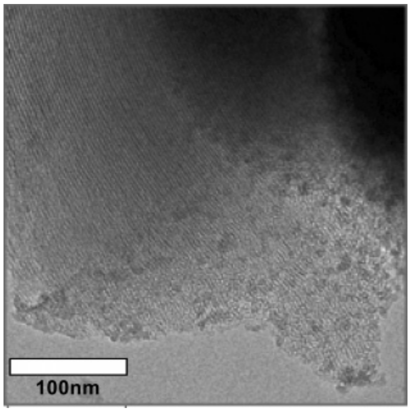


Figure 3. Transmission electron micrograph of sample VI.MCM.

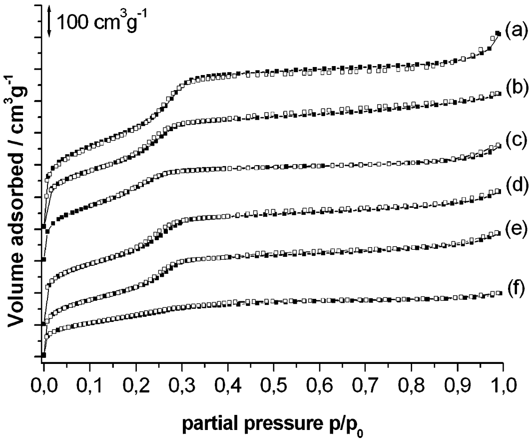


Figure 4. Nitrogen sorption isotherms of unmodified (a) MCM-41 and samples (b) VI.MCM, (c) ALY.MCM, (d) TMSAC.MCM, (e) PHAC.MCM, and (f) STYR.MCM (curves are offset from each other). Filled symbols, adsorption; empty symbols, desorption.

The presence of vinyl groups in the pores of MCM-41 is confirmed by the Raman bands of the olefinic C−H− and C═C− valence vibrations (Figure 6). These vibrations are located at $\nu_{CH} = 3069$ cm^{-1} and $\nu_{C=C} = 1603$ cm^{-1}. In

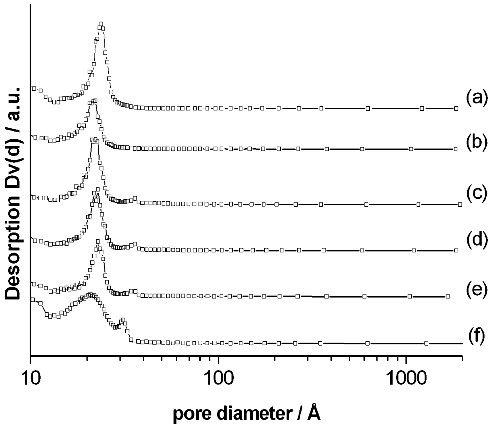


Figure 5. Pore size distributions of unmodified (a) MCM-41 and samples (b) VI.MCM, (c) ALY.MCM, (d) TMSAC.MCM, (e) PHAC.MCM, and (f) STYR.MCM.

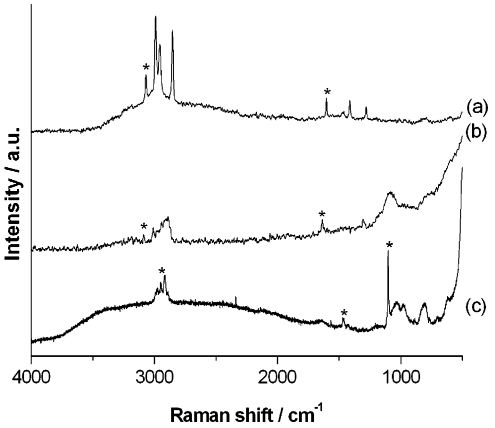


Figure 6. Raman spectra of samples (a) VI.MCM, (b) ALY.MCM, and (c) TMSAC.MCM. Bands referred to in the text are marked with an asterisk.

Table 2. Data Derived from Nitrogen Sorption Analysis

sample name	BET surface area ($m^2\ g^{-1}$)	pore volume ($cm^3\ g^{-1}$)	pore diameter (Å)
unmodified MCM-41	1150	0.81	23.9
VI.MCM	803	0.60	22.1
ALY.MCM	829	0.50	21.5
TMSAC.MCM	889	0.61	22.4
PHAC.MCM	829	0.55	23.1
STYR.MCM	474	0.30	21.1

contrast, the bands of the allyl groups introduced into the mesoporous structure are located at $\nu_{CH} = 3088\ cm^{-1}$ and $\nu_{C=C} = 1636\ cm^{-1}$ (Figure 6). These signatures allow us to differentiate between the two hybrid materials.

A further characteristic that differs between grafted vinyl and allyl groups anchored to mesoporous silica can be observed by measuring ^{13}C MAS NMR spectra. By carrying out the reaction of the allylic Grignard reagent with MCM-41 at +68 °C, an isomerization of the olefinic carbons was detected (Figure 7). It appears that the allyl group can undergo a side reaction, the so-called 1,3-sigmatropic shift, resulting in a terminal or an internal olefin.[28] Although reaction at room temperature yields the terminal olefin as the single product, at higher temperatures, a mixture of both olefins is obtained. Because the internal olefin is not observed at room temperature or lower temperatures, this rearrangement is probably thermally induced. This temperature dependence demonstrates one of the key advantages of the metal−organic functionalization route, which is the option to control the reaction temperature over a wide range, especially at low temperatures. Thus, thermally induced isomerizations and decompositions can be avoided, e.g., by performing the functionalization at −78 °C in a dry ice acetone bath.

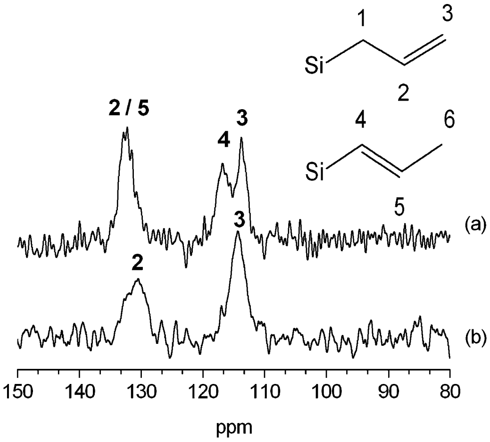


Figure 7. ^{13}C MAS NMR spectra of the compound ALY.MCM synthesized at (a) 68 and (b) 25 °C.

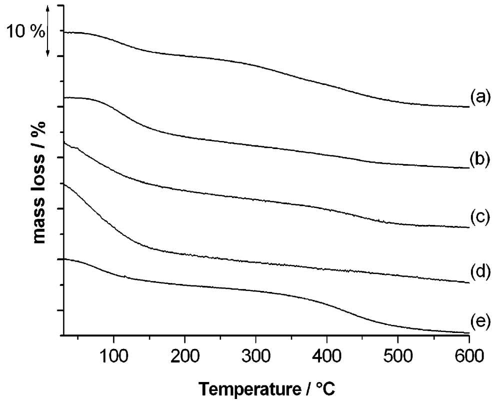


Figure 8. TGA data of the samples (a) VI.MCM, (b) ALY.MCM, (c) TMSAC.MCM, (d) PHAC.MCM, and (e) STYR.MCM (curves are offset from each other).

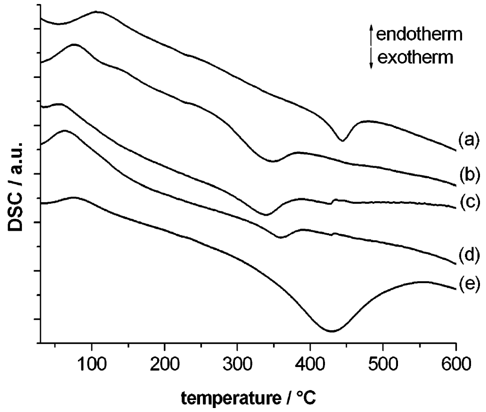


Figure 9. DSC data of the compounds (a) VI.MCM, (b) ALY.MCM, (c) TMSAC.MCM, (d) PHAC.MCM, and (e) STYR.MCM (curves are offset from each other).

As a further method to distinguish between the different incorporated organic moieties, combined thermogravimetric and calorimetric measurements were performed (Figures 8 and 9). These measurements were also analyzed to obtain

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Table 3. Organic Contents as Determined by TGA Mass Loss between 200 °C and 600 °C

sample name	g of organics/ g of silica	mmol of organics/ g of silica	yield (%)
VI.MCM	0.111	4.11	82
ALY.MCM	0.080	1.95	39
TMSAC.MCM	0.089	0.91	18
PHAC.MCM	0.077	0.76	15
STYR.MCM	0.104	1.00	20

the amount of incorporated organic material and the yield of the functionalization reaction (see Table 3). As can be expected for steric reasons, the amount of incorporated organic material is dependent on the size of the functional group. Although 4.11 mmol of vinyl groups per gram of silica (80% yield) are obtained for the functionalized material VI.MCM, this ratio was reduced to 1.95 mmol (40%) for the allylic system and 0.76−1.00 mmol (15−20%) for the three larger moieties.

All samples show a weight loss up to 100 °C in the TGA that corresponds to the release of water from the mesopores and results in an endothermic differential scanning calorimetry (DSC) signal. In contrast, decomposition of the organic groups by oxidation reactions results in exothermic peaks in the DSC curve. One might expect a clear difference in the thermal behavior of the double-bond systems VI.MCM and ALY.MCM in comparison with the triple-bond systems TMSAC.MCM and PHAC.MCM, as acetylenic compounds are usually more sensitive to oxidizing conditions in comparison to the related olefins.[29] However, there is no clear trend for the oxidation temperature. Both triple-bond systems TMSAC.MCM and PHAC.MCM show decomposition steps as exothermic reactions at temperatures of 338 and 360 °C, respectively. However, this step occurs for the double-bond system ALY.MCM in a similar temperature range at 348 °C. Only VI.MCM shows a clearly distinct behavior and is stable up to much higher temperatures of about 396 °C. The observed conditions for the oxidative decomposition of the organic functionalities apparently point to a more complex behavior, possibly related to the steric protection of the acetylenic compounds.

Raman spectroscopy was used in order to confirm the modification of mesoporous hosts with acetylenic groups. The phenyl group in PHAC.MCM could be characterized by the stretching vibrations of the aromatic ring and the deformation vibrations of the aromatic C−H bonds (Figure 10). They are located at $\nu_{C=C} = 1637$ cm^{-1} and $\delta_{CH} = 802$ cm^{-1}, respectively. In comparison, for TMSAC.MCM, the intense sharp band at $\nu_{SiC} = 1100$ cm^{-1} can be assigned to the stretching vibration of the silicon−carbon bond in the trimethylsilyl group (Figure 6). In addition, the C−H valence vibration of the methyl groups in TMSAC.MCM ($\nu = 2891$ cm^{-1}) and the C−H deformation vibration at $\delta_{CH} = 1458$ cm^{-1} are both typical for this compound. The intensity of the C−C triple bond mode is too weak to be detected in the Raman spectrum. This is typical for disubstituted acetylenes and related to the symmetry of the substitution.[30] However, given that the terminal groups, the trimethylsilyl group, and the phenyl ring, respectively, can be detected by Raman spectroscopy, the grafting of the two acetylenic compounds to the mesoporous host was proven.

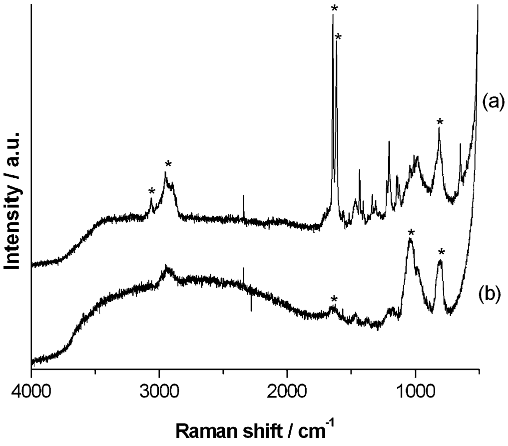

Figure 10. Raman spectra of samples (a) STYR.MCM and (b) PHAC-.MCM. Bands referred to in the text are marked with an asterisk.

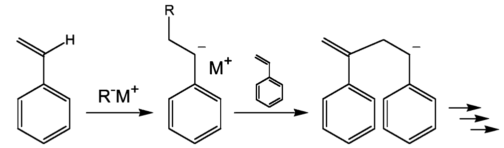

Figure 11. Reaction scheme of the anionic polymerization of styrene.

The characterization of STYR.MCM turns out to be straightforward. As styrene compounds can undergo anionic polymerization with anionic compounds such as *n*-butyl lithium, one would expect a complex mixture of products from a reaction at room temperature (Figure 11).[31] However, for the reaction performed at −78 °C, such a behavior could not be observed. On the basis of the nitrogen sorption analysis, the sample STYR.MCM shows a pore size distribution with an average diameter of about 2.1 nm, which is broadened in comparison to the other samples (Figure 5). This could be interpreted as an indication of styrene oligomers with different lengths occupying the pore system. However, this does not seem to be the case, as shown by TGA and Raman data, which will be discussed below. The difference is possibly caused by the metal−organic reagent, which consists of a more reactive lithiated species in the case of styrene and a Grignard reagent in the other cases. The sample possesses a specific surface area of 474 m^2 g^{-1} and a specific pore volume of 0.30 cm^3 g^{-1}, indicating a successful organic modification of the mesoporous silica. The reduced pore volume and the broader pore size distribution in comparison with the other samples could indicate some minor structural degradation as a result of the functionalization. The anchored organic groups could be clearly identified by Raman spectroscopy (Figure 10). Bands corresponding to the olefinic and aromatic C═C stretching vibrations are located at $\nu_{olef.} = 1641$ cm^{-1} and $\nu_{ar.} = 1611$ cm^{-1} in the Raman spectrum of STYR.MCM. Moreover, the olefinic and aromatic C−H valence vibrations can be associated with $\nu_{CH(ol)} = 3022$ cm^{-1} and $\nu_{CH(ar)} = 3061$ cm^{-1}.

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(29) Beyer, H.; Walter, W.; Francke, W. *Lehrbuch der Organischen Chemie*, 23rd ed.; S. Hirzel Verlag: Stuttgart, Germany, 1998; p 98.
(30) Socrates, G. *Infrared and Raman Characteristic Group Frequencies*, 3rd ed.; John Wiley & Sons: New York, 2001.
(31) Beyer, H.; Walter, W.; Francke, W. *Lehrbuch der Organischen Chemie*, 23rd ed.; S. Hirzel Verlag: Stuttgart, Germany, 1998; p 81.

The para-substitution of the vinyl group relative to the silicon atom on the ring in the anchored molecule is confirmed by the single band at $\delta_{CH} = 812$ cm^{-1} in the Raman spectrum. A single band in this region is typical for para-substituted aromatic molecules. The modified solid shows a high thermal stability up to about 400 °C and relatively rapid decomposition at about 430 °C, as indicated by a combined TGA/DSC measurement. This indicates that there are neither oligomers nor polymers inside the pores of STYR.MCM. This statement is supported by the data obtained from Raman spectroscopy. One would expect bands between $\nu = 1597$ cm^{-1} and $\nu = 1600$ cm^{-1} for the presence of polymerization products.[32] The absence of such bands in the spectrum of STYR.MCM strongly suggests that no polymerization occurred during the organometallic modification of the mesoporous host.

Conclusion

The metal−organic route for the modification of mesoporous silica has been used successfully for the introduction of multiply bonded systems into the porous structure of MCM-41. The anchored organic moieties include vinyl and allyl groups as well as different acetylenic groups and styrene. The modification reactions were followed by structural characterization methods as well as spectroscopic means, and clear evidence for the efficient anchoring reactions was obtained for these nanostructured inorganic−organic hybrid systems. It could be shown that the structural integrity of the mesoporous host is maintained during these modifications. The resulting reactive hybrid materials possess large surface areas and are promising candidates for a large variety of subsequent reactions in the channel system of the mesoporous host.

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(32) Crawford, K. D.; Hughes, K. D. *J. Phys. Chem. B* **1998**, *102* (13), 2325.