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Optimization of Reaction Conditions for the Metalorganic Modification of MCM-41

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The modification of periodic mesoporous silica with organic groups following an optimized metalorganic route is described. Organolithium and Grignard reagents (*n*-butyllithium and allyl-magnesium bromide) were used to directly substitute silicon atoms with organic moieties in the channel walls of the silica host. A detailed study of several representative reactions with respect to reaction parameters, that is, reaction temperature, reaction time, and reagent concentration, shows that the degree of surface substitution can be controlled within a broad range and up to very high levels while still maintaining the integrity of the ordered silica host. The functionalized mesoporous materials can also retain high surface areas and pore volumes. Furthermore, the reactions can be performed at low temperatures compared to the more traditional grafting techniques on the basis of organosilanes.

Introduction

The discovery of periodic mesoporous silica materials such as MCM-41 by Beck and co-workers in 1992[1,2] has led to a rapid development of a broad spectrum of mesoporous systems. Many of these materials exhibit two- or three-dimensional long-range order with respect to their nanoscale channel system. Their synthesis is usually based on cooperative self-assembly processes involving surfactants and framework building blocks.[3−6] These materials are expected to play an important role in the development of new catalysts and absorbents, for the immobilization of enzymes, as hosts in nanoparticle synthesis, and as membranes for ultrafiltration.[7−11] For many of these applications, the mesoporous materials are expected to show enhanced properties when their inner channel walls are functionalized with organic moieties.

Three general methods have been developed for the organic functionalization of the mesoporous materials. The first one is based on “postsynthesis grafting”.[12,13] For this approach, the presynthesized silica material is modified by the use of alkoxy- or chloro-organosilanes.[14,15] An alternative approach is based on the copolymerization of an organosilane with a silica precursor in the presence of the surfactant template.[16,17] This process is called co-condensation and requires the subsequent removal of the template, often by means other than calcination, to maintain the integrity of the desired organic moieties.[18,19] The latest method for the organic modification of mesoporous silica, on the basis of the substitution of silica with metalorganic compounds, was published by Yamamoto and Tatsumi in 2000.[20,21] While their original approach already showed promise for the organic modification of mesoporous silica, it also exhibited several drawbacks. One of them is the extension of the reaction time by a factor of 3 in comparison to classical techniques such as postsynthesis grafting. A further drawback is related to the two required steps of the reaction procedure. In contrast to classical methods, the required additional processing steps such as filtration, drying, solvent exchange, and washing lead to a complication of the modification procedure. Finally, the

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method often produces different organosilica surface species in the mesopores. The authors found doubly or triply alkylated surface silicon atoms in the material in addition to the desired monoalkylated silicon atoms, as shown by ^{29}Si-magic-angle spinning (MAS) NMR. To overcome these problems and to create a fast and economically attractive modification technique, Lim et al. and our group have independently developed a method to modify mesoporous silica materials in one-pot reactions.[22,23] The main aspect of the reaction, the direct conversion of surface silicon atoms in silica with a metalorganic reagent, has been reported long ago for the case of fumed silica by Kautsky and Bartocha and by Boehm et al. in 1955 and 1965, respectively.[24,25] They observed a direct conversion of silicon surface atoms by metalorganic compounds such as Grignard or organolithium compounds. The reaction is based on a direct attack of the nucleophile at the silicon atom of a siloxane bridge. However, the main products discussed in these publications were organosilanes or organosilanolates. The aspect of the organic modification of the silica surface was not presented in these publications because of the complete conversion of the metalorganic compounds to organosilanes. In our case, appropriate reaction conditions were found for the functionalization of the surface of the mesoporous material MCM-41 by use of metalorganic compounds such as Grignard or organolithium compounds, without destroying the ordered structure of the host.

In this article, we report a detailed study of the optimization of the reaction conditions for the metalorganic functionalization of mesoporous silica. The reaction conditions were investigated regarding reaction temperature, reaction time, and reaction stoichiometry to find the most efficient and economic conditions for the desired organic modification. Furthermore, we discuss the characterization of the products obtained from these reactions and the structural properties of the resulting mesoporous inorganic–organic hybrid systems.

Experimental Section

Procedure for the Synthesis of MCM-41. The quantity of 2.40 g (6.59 mmol) of hexadecyltrimethylammonium bromide (CTAB) was dissolved in 120 mL (6.67 mol) of water under stirring (200 rpm for 1 h).[26] The quantity of 9.85 mL (0.13 mol) of ammonia (25%) was added to the resulting suspension, and the whole mixture was stirred for an additional 5 min (200 rpm). After adding 10 mL (45.1 mmol) tetraethylorthosilicate (TEOS), the resulting suspension was stirred for 16 h at 200 rpm at room temperature. The colorless suspension was filtered and washed two times with 50 mL each of water and 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. We obtained 2.5 g MCM-41 as a colorless solid powder (93% conversion related to "Si" in TEOS).

Table 1. Reaction Conditions for the Alkylation of MCM-41: Varying the Reaction Time

entry	alkylation reagent [type/mmol][a]	temperature [°C]	time [h]	solvent [type/mL][b]	product
1	*n*-BuLi/5	25	2	hexane/20	BU.MCM **3**
2	*n*-BuLi/5	25	4	hexane/20	BU.MCM **1**
3	*n*-BuLi/5	25	6	hexane/20	BU.MCM **4**
4	*n*-BuLi/5	25	8	hexane/20	BU.MCM **5**
5	*n*-BuLi/5	25	16	hexane/20	BU.MCM **6**
6	*n*-BuLi/5	25	24	hexane/20	BU.MCM **7**
7	allylMgBr/5	25	2	THF/20	ALY.MCM **8**
8	allylMgBr/5	25	4	THF/20	ALY.MCM **2**
9	allylMgBr/5	25	6	THF/20	ALY.MCM **9**
10	allylMgBr/5	25	8	THF/20	ALY.MCM **10**
11	allylMgBr/5	25	16	THF/20	ALY.MCM **11**
12	allylMgBr/5	25	24	THF/20	ALY.MCM **12**

[a] In mmol akylation agent per gram of MCM-41. [b] Volumes given per gram of MCM-41.

Table 2. Reaction Conditions for the Alkylation of MCM-41: Varying the Reaction Temperature

entry	alkylation reagent [type/mmol][a]	temperature [°C]	time [h]	solvent [type/ mL][b]	product
1	*n*-BuLi/5	−78	4	hexane/20	BU.MCM **13**
2	*n*-BuLi/5	−20	4	hexane/20	BU.MCM **14**
3	*n*-BuLi/5	25	4	hexane/20	BU.MCM **1**
4	*n*-BuLi/5	68	4	hexane/20	BU.MCM **15**
5	allylMgBr/5	−78	4	THF/20	ALY.MCM **16**
6	allylMgBr/5	−20	4	THF/20	ALY.MCM **17**
7	allylMgBr/5	25	4	THF/20	ALY.MCM **2**
8	allylMgBr/5	68	4	THF/20	ALY.MCM **18**

[a] In mmol alkylation agent per gram of MCM-41. [b] Volumes given per gram of MCM-41.

Table 3. Reaction Conditions for the Alkylation of MCM-41: Varying the Concentration of Alkylating Agent

entry	alkylation reagent [type/mmol][a]	temperature [°C]	time [h]	solvent [type/ mL][b]	product
1	*n*-BuLi/2.5	25	4	hexane/20	BU.MCM **19**
2	*n*-BuLi/5	25	4	hexane/20	BU.MCM **1**
3	*n*-BuLi/10	25	4	hexane/20	BU.MCM **20**
4	*n*-BuLi/15	25	4	hexane/20	BU.MCM **21**
5	*n*-BuLi/20	25	4	hexane/20	BU.MCM **22**
6	allylMgBr/2.5	25	4	THF/20	ALY.MCM **23**
7	allylMgBr/5	25	4	THF/20	ALY.MCM **2**
8	allylMgBr/10	25	4	THF/20	ALY.MCM **24**
9	allylMgBr/15	25	4	THF/20	ALY.MCM **25**
10	allylMgBr/20	25	4	THF/20	ALY.MCM **26**

[a] In mmol alkylation agent per gram of MCM-41. [b] Volumes given per gram of MCM-41.

General Procedure for the Metalorganic Modification of MCM-41. The quantity of 0.25 g of MCM-41 was dried at 150 °C for 15 h under vacuum. The material was cooled down to room temperature and was suspended in 5 mL THF (allyl compounds) or *n*-hexane (butyl compounds) under a nitrogen atmosphere and was stirred for 15 min at ambient temperature. The respective suspension was heated or cooled to the desired temperature (Tables 1−3). To the resulting suspensions, between 1.25 and 5 mmol of the respective metalorganic compound was added (Table 1−3). The suspensions were stirred at the elevated temperature for the times given in Tables 1−3. After reaction, all samples were hydrolyzed by adding methanol and water, were filtered, and were washed with 100 mL each of water and ethanol, respectively. The precleaned solids were dried in air overnight. The final purification step of the solids was performed by Soxhlet extraction with methylene chloride.

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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 a 30-point BET measurement at pressure values p/p_0 smaller than 0.3. Pore diameters were determined 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). X-ray diffraction (XRD) patterns were recorded on a Scintag XDS 2000 powder diffractometer using the Cu K_α line ($\lambda = 0.15405$ nm). ^{29}Si-MAS NMR spectra were recorded on a Bruker DSX Avance 500 FT-NMR using cross polarization. Transmission electron microscopy (TEM) micrographs were taken on a JEOL JEM 2010 transmission electron microscope at a voltage of 200 kV. TEM samples were prepared by redispersing about 1 mg material in 5 mL ethanol by ultrasonication for 30 min and transferring one drop of the resulting suspension on a carbon-coated copper grid. Thermogravimetric analysis (TGA) measurements were performed on a Netzsch STA 440 C TG/DSC by heating 10 mg sample with a heating rate of 10 °C per minute in a stream of synthetic air (25 mL per minute flow rate).

Results and Discussion

Reaction Time. The first investigation was focused on the dependence of the structural stability and the surface coverage on the reaction time of the metalorganic compound with the MCM-41 host. The parameter range was defined by the concentration of the alkylating agent, the reaction temperature, the amount of solvent, and the reaction time. As one can see in Table 1, all of the parameters except the reaction time were initially kept constant. The reaction time was varied in six steps from 2 to 24 h. These conditions were used for *n*-butyl modifications and for allyl modifications. The predominant characterization at this stage was done by TGA/differential scanning calorimetry (DSC) and nitrogen sorption data. TGA data were used to determine the content of organic molecules in the structure in millimol per gram of modified MCM-41. The decrease of the specific surface area because of the modification was calculated on the basis of nitrogen sorption data using the BET theory.[27] Further structural aspects of the resulting inorganic−organic hybrid structures were addressed by X-ray diffraction and transmission electron microscopy (TEM). The changes regarding specific surface area and surface coverage because of the variation of the reaction time are given in Figure 1 and Figure 2 for the modifications with both *n*-butyl-lithium and allyl-magnesium bromide, respectively. The increase in reaction time leads to a decrease in specific surface area and an increase in surface coverage for both types of materials. The decrease in surface area progresses fast during the first 8 h of reaction and proceeds at a slower rate afterward for both allyl- and *n*-butyl-functionalized samples. This suggests the existence of sites with different reactivity, that is, easily accessible/reactive sites at the silica surface where the substitution occurs quickly and less accessible sites which are subsequently attacked by the metalorganic species, for example, by breaking siloxane rings at the boundary of the silica framework. This assumption is supported by the fact that the surface areas obtained after saturation are different for both types of samples. The surface areas of samples functionalized with the smaller allyl group remain at about 500 m^2/g after the first rapid decrease, while the surface area of samples with the larger butyl group (which behaves similarly in the beginning of the reaction) remains at values around 350 m^2/g. On the other hand, the surface coverage keeps increasing also at longer reaction times. While the progress is almost constant in the case of the allyl-Grignard reagent, it shows a strong increase in the case of butyl lithium after 8 h which also corresponds to the greatest loss in surface area. This could be caused by the higher reactivity of lithiated species as compared to Grignard reagents, which allows the butyl lithium to more effectively create new reaction sites. However, the increasing coverage and the resulting decrease of the specific surface area do not seem to negatively influence the integrity of the structure at short reaction times. This could be demonstrated by X-ray diffraction presented in Figure 3. One observes a clear loss in scattering contrast in the structure by increasing the reaction time, as indicated by the decrease of the intensity of the (100) peak. This is based on the increasing coverage of the pore walls with organic molecules that leads to a loss in contrast between the pore walls and the pore. Furthermore, a slight broadening of the (100) reflection is observed with increasing reaction times which indicates that the metalorganic species attacking the silica walls produce some irregularities in the ordered porous framework. The (100) reflection is still present even after a reaction time of 24 h, but the intensity is very low

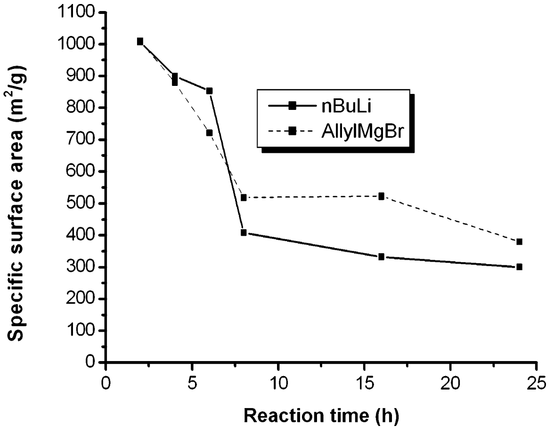

Figure 1. Changes in the specific surface area obtained by varying the reaction time.

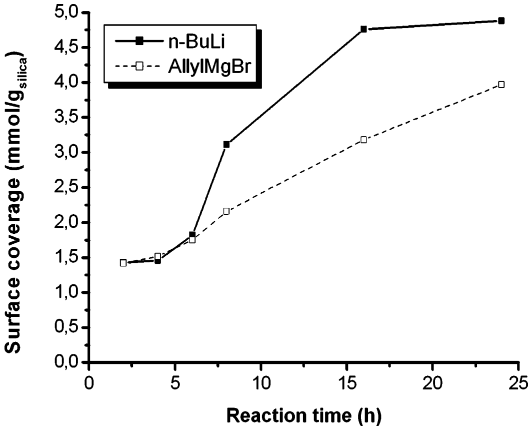

Figure 2. Changes in the surface coverage obtained by varying the reaction time.

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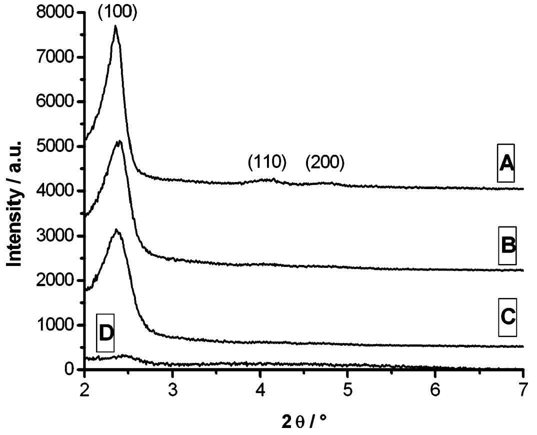

Figure 3. Changes in intensity of the (100) reflection of the starting material MCM-41 (A) and of BU.MCM samples obtained by varying the reaction time: BU.MCM **1** (4 h) (B), BU.MCM **4** (6 h) (C), and BU.MCM **7** (24 h) (D) (graphs are offset along the *y*-axis for clarity).

and is shifted to smaller lattice distances, which most likely indicates some loss of structure leading to a contraction of the framework. By comparison of TEM images of the parent material MCM-41 with an inorganic−organic hybrid material, one can still see the intact structure of the mesoporous silica after short reaction times (Figure 4).

Assuming a homogeneous coverage of the pore walls with organic moieties, the surface area of calcined MCM-41 samples should decrease from ~1200 m^2/g to values of about 900−1000 m^2/g because of the decrease in pore size after butyl and allyl functionalization, respectively. This is the case for short reaction times, that is, after 4 h, as can be seen in Figure 1. Nevertheless, the structural integrity and specific surface area are eventually reduced by a further increase of the reaction time. Therefore, while there is a certain tolerance in considering the optimum reaction time, we have chosen a reaction time of 4 h for further investigations which yields materials with substantial organic functionalization (about 1.25 $\mu mol/m^2$) but at the same time causes only small losses in surface area. This is based on the desired creation of high surface area inorganic−organic hybrid materials, one of the leading criteria in applications such as catalysis, sensing, and chromatography. The organic content achieved under these conditions was found to be significant, with a content of 1.31 mmol/g for BU.MCM **1** and 1.25 mmol/g for ALY.MCM **2**.

Reaction Temperature. The second parameter to be studied was the reaction temperature. In comparison to the classical modification technique “postsynthesis grafting”, the reduction of the reaction temperature helps to reduce energy consumption as well as the complexity of the process. More importantly, compounds that are sensitive to elevated temperature could be handled without problems. To examine this parameter, we kept the reaction time, the concentration of alkylating agent, and the type and amount of solvent constant. The reaction was performed at temperatures ranging from −78 °C to +68 °C (reflux temperature of THF). The exact parameters are listed in Table 2. The resulting changes regarding the specific surface area and the organic coverage of the mesoporous channel surface are shown in Figure 5 and Figure 6. The reactivity of the metalorganic reagents is high enough to convert the pure silica host into an inorganic−organic hybrid material even at extremely low temperatures as can be seen by the almost constant surface coverage for *n*-butyl lithium functionalized samples in the range of −78 °C to 25 °C. Samples functionalized by Grignard reagents, however, show a higher dependency on reaction temperature which is likely related to their lower reactivity in comparison to lithiated metalorganics. However, there is a clear tendency for a strong increase of surface coverage for both metal organic reagents by increasing the temperature to the upper limit, which in the case of *n*-butyl lithium leads to values of 4.2 mmol/g. Under such reflux conditions, however, the decrease in specific surface area is too drastic to be used in standard modifications (331 m^2/g for BU.MCM **15**). Comparing the specific surface area and the organic content of all samples for reactions done at −78, −20, and +25 °C, we found just moderate differences regarding surface area and organic loading ($\Delta(\text{area})_{max} = 110\ m^2/g$; $\Delta(\text{loading})_{max} = 0.58$ mmol/g). As the reactions at low temperatures need cooling agents such as an acetone/dry ice bath, carrying out the reaction at room temperature is clearly preferable. Further structural information as to the nature of the reaction products is obtained by solid-state NMR spectroscopy. The ^{29}Si-MAS NMR data provide clear evidence for the increased formation of Si−C bonds by increasing the reaction temperature. As shown in Figure 7, at −78 °C there are only so-called T^3-species (singly substituted organic) to be found in the spectrum albeit at a low ratio in comparison to the silicon framework atoms composed of Q^3 and Q^4 species. By increasing the reaction temperature to −20 °C, we found an increased ratio of T^3 species relative to the framework silicon atoms and also the appearance of D^2-species (−20 ppm). These double-alkylated silicon atoms could have a negative influence on potential catalytic applications because of the crowding of functional groups on one silicon atom. The intensity of the D^2 peak is strongly increasing under reflux conditions. As the signal for the T^3 species is also increasing, these reaction conditions can be used if a high surface coverage is desired. However, under these conditions, one has to accept a certain loss in the integrity of the mesoporous structure. This is based on X-ray analysis and nitrogen sorption data of the samples BU.MCM **1** (synthesized at room temperature) and BU.MCM **15** (synthesized at +68 °C). By comparing the diffractograms of BU.MCM **1** and BU.MCM **15**, a strong loss in intensity of the (100) reflection can be observed. Furthermore, the (110)- and (200)-reflections could not be indexed in BU.MCM **15** (Figure 8). As the decreased intensity of the reflection could be caused either by a loss of X-ray contrast because of extended functionalization or by a loss of structural integrity, the functionalized materials were further studied with nitrogen sorption (Figure 9). Showing both lower specific surface area and reduced pore volume, the sample BU.MCM **15** also exhibits a significant broadening and decrease of the maximum of the pore size distribution, in contrast to sample BU.MCM **1**. As a well-defined pore size distribution is one of the characteristics of periodic mesoporous materials such as MCM-41, one would expect that the integrity of the mesoporous structure was partially damaged under reflux conditions, leaving the resulting material almost nonporous.

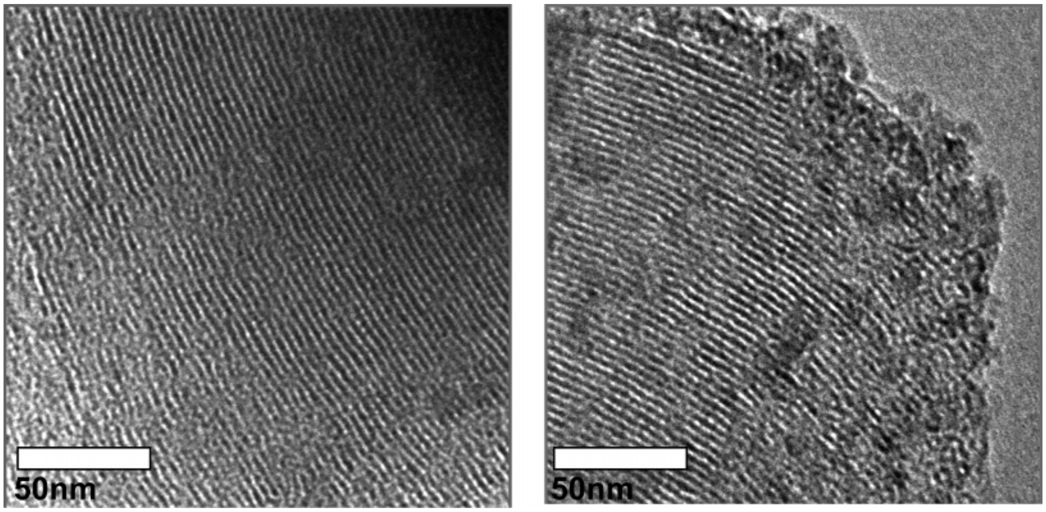

Figure 4. TEM images of the starting material MCM-41 (left side) and the modified material BU.MCM **1** (right side) after 4 h reaction time.

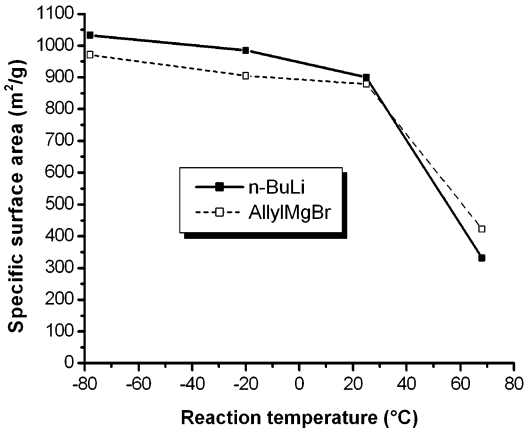

Figure 5. Changes in specific surface area by varying the reaction temperature.

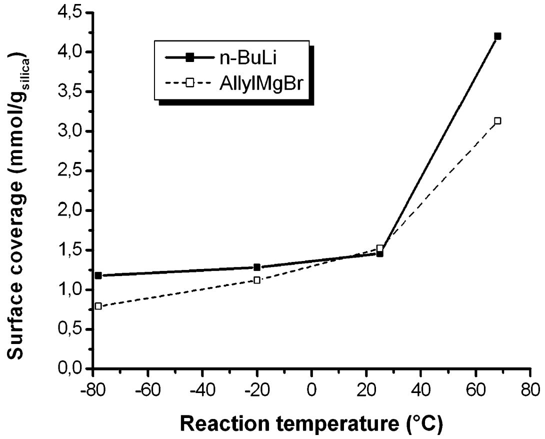

Figure 6. Changes in surface coverage by varying the reaction temperature.

On the basis of the above studies, two of the reaction parameters for further experiments can be fixed at an optimum value. The last parameter to be examined is the dependence of the reaction on the concentration of alkylating agents. It was of interest to determine the minimal useful amount of alkylating agent. For this purpose, we used concentrations ranging from 2.5 mmol to 20 mmol of alkylating agent per gram of MCM-41 (Table 3). Again, we observed clear trends regarding the increase of the surface coverage and the decrease of the specific surface area with an increase of the concentration of alkylating agent. The integrity of the structure of the new inorganic−organic hybrid materials was investigated by comparison of organic content

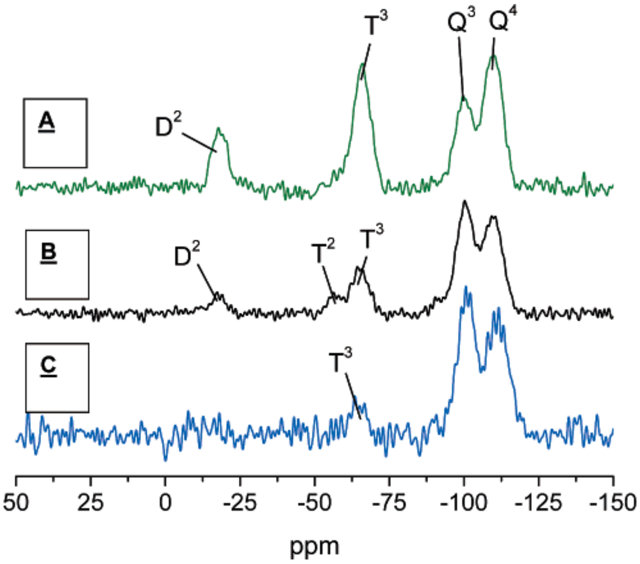

Figure 7. ^{29}Si-MAS NMR spectra of BU.MCM samples synthesized at temperatures of +68 °C (A), room temperature (B), and −78 °C (C) (graphs are offset along the *y*-axis for clarity).

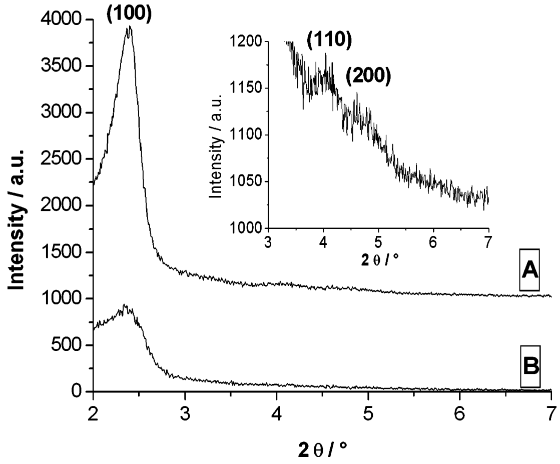

Figure 8. X-ray powder patterns of samples BU.MCM **1** (A) and BU.MCM **15** (B). Insert: Enlargement of the area from 2 to 7° 2θ from sample BU.MCM **1** (graphs are offset along the *y*-axis for clarity).

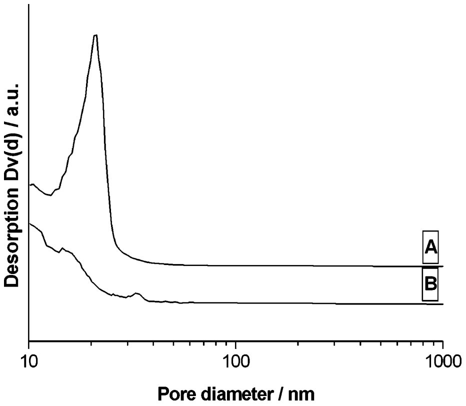

Figure 9. Pore size distribution of the samples BU.MCM **1** (A) and BU.MCM **15** (B) (graphs are offset along the *y*-axis for clarity).

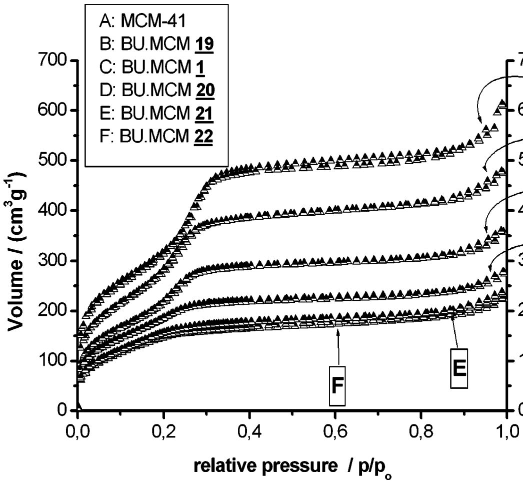

Figure 10. Changes in the isotherms of organically modified materials as a function of the concentration of alkylating agent.

and the adsorption isotherms of the synthesized materials. All of the isotherms exhibit the typical shape of a type IV isotherm (Figure 10). One can identify the significant decrease of the pore volume associated with the increase of organic loading. Furthermore, we found a shift of the inflection point in the isotherm down to lower p/p_0 values for increasing organic content. This shift is due to the reduction of the pore diameter on the basis of the increasing organic modification of the pore walls. The data presented here are in good agreement with the values for organic loading shown in Figure 11. Although the surface coverage could be increased to 2 mmol of organic groups per gram silica by using a concentration of 20 mmol alkylating agent, we defined a concentration of 5 mmol metalorganic compound per gram of MCM-41 as an optimized standard concentration for the modification of mesoporous silica. This choice is based on two aspects. First, it is desirable to use only a small amount of metalorganic compound from an economic point of view. The second aspect is focused on the strong reduction of the surface area below values of 600 m^2/g when using a large excess of alkylating agent. The retention of high surface areas is an important factor in designing synthetic methods for the functionalization of mesoporous materials.

It should also be taken into account that the yield of functional groups in relation to deployed metalorganic reagent decreases for higher concentrations, which can be important from an economical point of view. While for smaller concentrations of 2.5 mmol alkylating agent per gram silica about 50% of the reactant molecules attach themselves to the silica surface, this yield is reduced to ~25% at 5 mmol/g silica and to ~10% for higher concentrations of 10, 15, and 20 mmol/g silica.

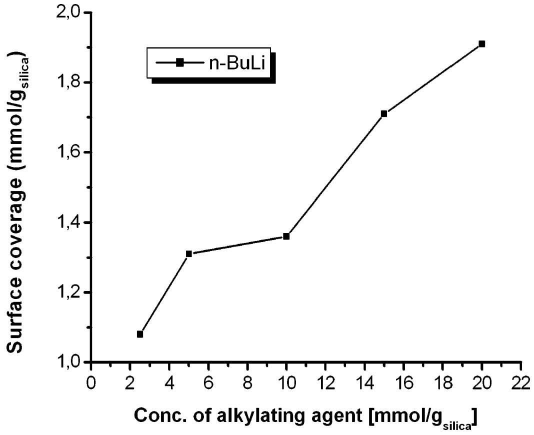

Figure 11. Changes in surface coverage as a function of the concentration of alkylating agent.

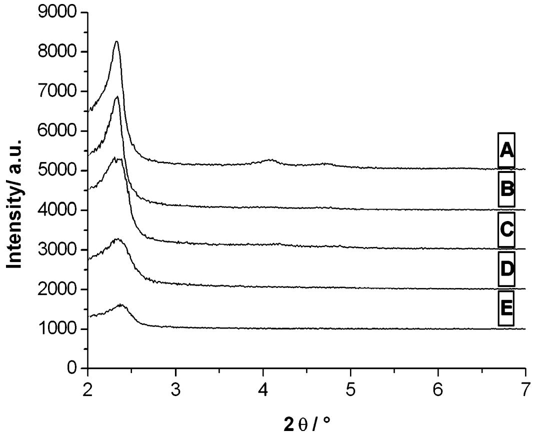

Figure 12. X-ray powder patterns of BU.MCM samples obtained by varying the concentration of alkylating agent: BU.MCM **19** (A), BU.MCM **1** (B), BU.MCM **20** (C), BU.MCM **21** (D), and BU.MCM **22** (E) (graphs are offset along the *y*-axis for clarity).

Analysis of the XRD patterns reveals that higher concentrations of alkylating agent lead to a decrease in intensity of the (100) reflection, which could be caused either by loss of X-ray contrast or loss of long-range order (Figure 12). The reflection is also noticeably broadened and right-shifted to smaller lattice plane distances with increasing alkylating agent concentrations, which suggests at least a partial loss of structural integrity. To further elucidate the possible degeneration of the porous network, the pore size distributions calculated from nitrogen sorption measurements were analyzed (Figure 13). As expected, the pore size is significantly decreased by metalorganic functionalization of the pore walls. However, higher concentrations of alkylating agent also lead to a broadening and ultimately to a loss of defined pore size distributions, indicating a strong decrease in structural order for these samples. It is therefore concluded that only moderate amounts of metal organic reagent should be applied for functionalization as their high reactivity allows

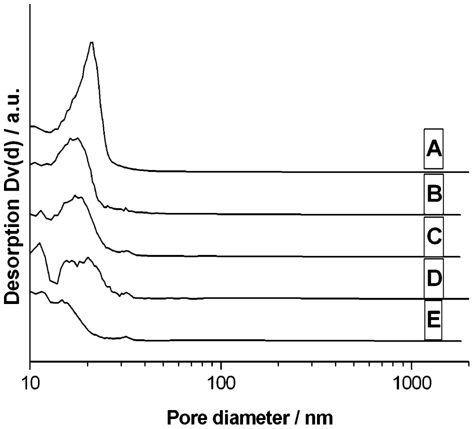

Figure 13. Pore size distributions of BU.MCM samples obtained by varying the concentration of alkylating agent: BU.MCM **19** (A), BU.MCM **1** (B), BU.MCM **20** (C), BU.MCM **21** (D), and BU.MCM **22** (E) (graphs are offset along the *y*-axis for clarity).

them to directly attack and disrupt the ordered silica structure at higher concentrations.

Conclusions

The results discussed in this article show the flexibility of the metalorganic route for the organic modification of mesoporous silica. The reaction can be performed at very low temperatures compared to the more traditional grafting techniques based upon organosilanes. This feature can be very attractive when considering the grafting of chemically sensitive molecules to the silica surface. Furthermore, the insights obtained with regard to the effect of reaction temperature, reaction time, and reagent concentration show that one can control the degree of surface substitution within a broad range and up to very high levels. Finally, as numerous organic compounds can be prepared as lithiated or Grignard reagents, the metalorganic route offers an enormous diversity for the grafting chemistry in mesoporous silica. We will report on this diversity in the near future.

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Supporting Information Available: ^{29}Si-MAS NMR spectra of samples ALY.MCM **16**−**18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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