



Modification of Surface and Structural Properties of Ordered Mesoporous Silicates

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Abstract. Two simple modification methods for ordered mesoporous silicas were examined and compared. MCM-41 molecular sieve was physically coated with 4'-cyano-4-biphenyl [4(4-pentenylloxy)]benzoate (CBPB) and chemically modified using trimethylethoxysilane. The structural and surface properties of the obtained materials were characterized using elemental analysis, thermogravimetry and nitrogen adsorption over a wide pressure range.

It was shown that the pore size of the MCM-41 material was not decreased significantly after the coating procedure, even for high loadings of CBPB. Moreover, low pressure adsorption measurements indicated that significant fractions of the MCM-41 surface were not covered by CBPB, even for high CBPB loadings, which suggests that the attained coverage may be very nonuniform. The chemical bonding procedure led to a marked decrease in the pore size and change of surface properties.

It was demonstrated that nitrogen adsorption measurements provide a means of a thorough characterization of modified MCM-41 materials, allowing to estimate the surface area, pore volume and pore size distribution. Moreover, low pressure adsorption data can be used to qualitatively or semiquantitatively assess the surface coverage of the coated/bonded organic groups, which may be used to estimate the uniformity of the coverage and therefore, the usefulness of the modification procedure.

Keywords: mesoporous molecular sieves, chemical modification, coating, nitrogen adsorption, structural characterization of adsorbents

Introduction

After the discovery of M41S mesoporous molecular sieves (Beck et al., 1992), a significant effort has been made to engineer their structural and surface properties (Sayari, 1996a, b). One of the members of the M41S family, namely MCM-41, which exhibits long cylindrical pores arranged in a hexagonal pattern, attracted particular attention and was the subject of far more studies than any other periodic mesoporous structure (Sayari, 1996a, b). The pore size of MCM-41 materials can be tailored in the range from ca. 2 to 10 nm by choosing surfactants of a proper chain length (Beck et al., 1992; Kruk et al., 1997b) or adding expander

molecules during the synthesis (Beck et al., 1992). Alternatively, a postsynthesis hydrothermal treatment can be used (Khushalani et al., 1995; Sayari et al., 1997; Huo et al., 1996). The above methods allow to engineer the porous structure of MCM-41 molecular sieves, but essentially do not influence the surface properties of the obtained materials. In order to tailor the surface properties, various heteroatoms, such as titanium or vanadium can be incorporated into the siliceous walls of MCM-41, inducing desirable (e.g., catalytic) properties (Sayari, 1996a and references therein). One can also take advantage of the rich surface chemistry of silica (Vansant et al., 1995) and bond organic ligands (Beck et al., 1992; Brunel et al., 1995; Feng et al.,

1997) or anchor inorganic species (see review articles by Sayari, 1996a, b). Such modifications change the surface properties of MCM-41, but also may lead to a significant decrease of the pore size.

Chemical modifications and physical coating of the silica surface were shown to be very useful, leading to materials with engineered surface properties suitable for advanced applications, especially in the field of mixture separation and purification (Vansant et al., 1995), where high performance liquid chromatographic separations can serve as the best example (Scott, 1993). Therefore, it is surprising that there are only few reports of such modifications for novel mesoporous molecular sieves (Beck et al., 1992; Brunel et al., 1995; Feng et al., 1997). The current study was intended to explore the simplest methods of modification of the surface and pore structure of MCM-41 molecular sieves, i.e., chemical bonding of small nonpolar ligands and physical coating. Another crucial point of the study was to test nitrogen adsorption methods of characterization for modified siliceous mesoporous materials and to show their usefulness in monitoring changes in surface and structural properties. Therefore, the current work was performed to provide a solid foundation for further modifications of MCM-41 materials in order to improve their hydrothermal stability (Ryoo and Jun, 1997) and structural and surface properties, with the ultimate goal at developing novel materials for advanced applications.

Materials and Methods

Materials

4'-cyano-4-biphenyl[4-(4-pentenyl)oxy] benzoate (CBPB) was synthesized as reported previously (Zhou et al., 1994). Trimethylethoxysilane was acquired from United Chemical Technologies, Inc. (Bristol, PA, USA). The synthesis and properties of the MCM-41 molecular sieve used in the current study were described in detail elsewhere (Kruk et al., 1997b, Kruk et al., 1997c). The X-ray diffraction interplanar spacing d_{100} of the sample was equal to 3.87 nm. The MCM-41 material was modified by either physical coating with CBPB or chemical bonding of trimethylethoxysilane. In the coating procedure, the MCM-41 silicate was added to a chloroform solution containing a proper amount of CBPB. Subsequently, the solvent was removed using a rotary evaporator at 313 K and the coated MCM-41 was dried overnight in an oven at 323 K. The chemically modified sample was synthesized as

follows. The MCM-41 material was exposed to water vapor in a desiccator for 20 h prior to the synthesis. Then, the sample was added to dry toluene and the mixture was stirred for 15 min. Subsequently, trimethylethoxysilane was added and the mixture was refluxed at 393 K for 6 h. The product was washed with dry toluene and acetone and dried under vacuum for 12 h. The samples will be denoted as follows. The unmodified MCM-41 molecular sieve will be referred to as MCM-41. The physically coated samples will be designated as $X\%$ CBPB-MCM-41 or simply $X\%$ CBPB, where X stands for the weight percent of CBPB in the obtained materials. The chemically modified MCM-41 will be denoted as TMS-MCM-41.

Measurements and Calculation Methods

Nitrogen adsorption measurements were carried out on an ASAP 2010 volumetric adsorption analyzer from Micromeritics (Norcross, GA, USA). The MCM-41 and the modified samples were outgassed for 2 h at 473 and 413 K, respectively. The contents of carbon in the modified samples were obtained using a LECO CHNS-932 elemental analyzer (St. Joseph, MI, USA). The weight loss curves were recorded on a TGA 2950 high resolution thermogravimetric analyzer from TA Instruments, Inc. (New Castle, DE, USA).

The specific surface area S_{BET} was obtained from the BET method (Gregg and Sing, 1982; Rouquerol et al., 1994). The relative pressure intervals of 0.06–0.25, 0.04–0.14 and 0.03–0.1 were used in calculations for the MCM-41, CBPB-MCM-41 and TMS-MCM-41, respectively, to exclude data affected by the onset of condensation in the primary mesopores (Kruk et al., 1997b). It should be noted that according to IUPAC recommendations (Rouquerol et al., 1994), pores are classified as micropores (width < 2 nm), mesopores ($2 \text{ nm} < \text{width} < 50 \text{ nm}$) and macropores (width $> 50 \text{ nm}$). Moreover, in the current study, ordered mesopores of the materials are referred to as primary mesopores, whereas other mesopores (and macropores) are referred to as secondary mesopores.

The external (secondary mesopore) surface area S_{ex} and primary mesopore volume V_p of the samples were calculated using the α_s -plot method (Gregg and Sing, 1982; Kaneko et al., 1992; Sayari et al., 1997). A macroporous LiChrospher Si-1000 silica gel (EM Separations, Gibbstown, NJ, USA) was used as the reference adsorbent. In the α_s -plot method, the amount adsorbed for a solid under study is plotted as a function of the standard reduced adsorption α_s for the reference

solid (α_s is defined as the amount adsorbed on the reference adsorbent divided by the amount adsorbed on it at a relative pressure of 0.4). A high pressure linear part of the α_s -plot (α_s between 1.2 and 1.8, i.e., relative pressure from 0.6 to 0.87) was used to calculate S_{ex} from the slope of the line and to obtain V_p from its intercept with the "Amount Adsorbed" axis. The total pore volume V_t was assessed from the volume of nitrogen adsorbed at a relative pressure p/p_0 of 0.99 by converting it to the volume of liquid nitrogen at 77 K.

Pore size distributions were calculated from adsorption branches of the isotherms using the BJH method (Barrett et al., 1951) with the experimental statistical film thickness curve and the modified Kelvin equation for nitrogen adsorption in cylindrical pores (Kruk et al., 1997c). The latter method was shown to allow for an accurate assessment of the pore size for MCM-41 molecular sieves within a wide range of pore sizes (Kruk et al., 1997c). The modified Kelvin equation assumes the form: $r(p/p_0)$ [nm] = $2\gamma V_L/[RT \ln(p_0/p)] + t(p/p_0) + 0.3$, where r is the pore radius, V_L is the molar volume of liquid adsorbate, γ is its surface tension, R is the universal gas constant, T is the absolute temperature ($T = 77$ K), p is equilibrium pressure and p_0 is the saturation vapor pressure. The t -curve $t(p/p_0)$ was based on the adsorption isotherm for a macroporous silica gel, but it is accurately represented in the interval from 0.1 to 0.95 p/p_0 by the Harkins-Jura equation $t(p/p_0)$ [nm] = $0.1(60.65/(0.03071 - \log(p/p_0)))^{0.3968}$.

Adsorption energy distributions (AEDs) were obtained by inversion of the integral equation for the overall adsorption with respect to the AED (Jaroniec and Madey, 1988) using the INTEG program (Szombathely et al., 1992) based on the regularization method. The local adsorption behavior was described by the Fowler-Guggenheim isotherm (Kruk et al., 1997a). The number of nearest neighbors and their interaction energy (divided by the Boltzmann constant) were set to 4 and 95 K, respectively. Random topography of the adsorption sites was assumed (Jaroniec and Madey, 1988; Szombathely et al., 1992).

The weight percent WP of species introduced during the modification was calculated using the contents of carbon obtained from the elemental analysis, with the exception of 36% CBPB-MCM-41, for which the amount of CBPB was assessed from the thermogravimetry data. Subsequently, S_{BET} of the unmodified MCM-41 and WP were used to calculate the surface coverage SC of the species. The surface coverage SC_{ads}

of CBPB was also obtained from low pressure adsorption data.

Results and Discussion

Adsorption isotherms for the samples under study are shown in Fig. 1. Information about structural and surface properties is provided in Table 1. Previous studies

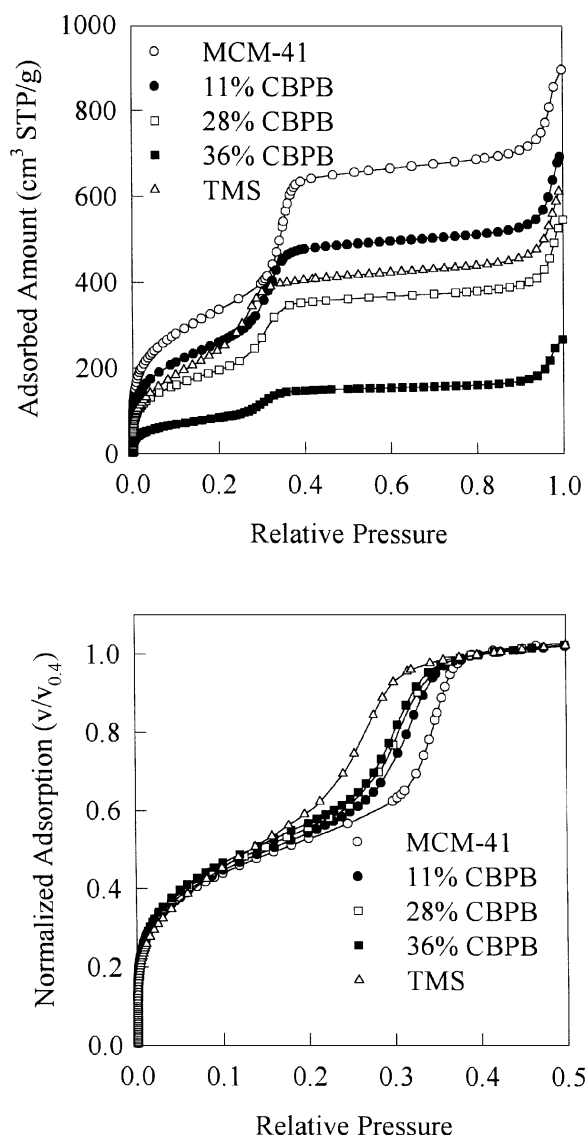


Figure 1. Nitrogen adsorption isotherms (top graph) for the samples under study. On the bottom graph, the adsorbed amounts were divided by the adsorbed amount at a relative pressure of 0.4 to allow for a better comparison of steps of nitrogen condensation in primary mesopores.

Table 1. Structural and surface properties of the samples under study.

Sample	S_{BET} (m ² /g)	S_{ex} (m ² /g)	V_p (m ³ /g)	V_t (m ³ /g)	w_{BJH} (nm)	WP (%)	SC (μmol/m ²)	SC_{ads} (μmol/m ²)
MCM-41	1240	180	0.92	1.38	3.81	—	—	—
11% CBPB	940 (1060)	130	0.68 (0.77)	1.08 (1.21)	3.61	11	0.27	<0.32
28% CBPB	710 (990)	120	0.50 (0.69)	0.82 (1.14)	3.57	28	0.86	<0.40
36% CBPB	310 (480)	70	0.20 (0.31)	0.42 (0.66)	3.49	36*	1.1	<0.48
TMS-MCM-41	820 (940)	140	0.56 (0.65)	0.95 (1.09)	3.29	12	1.6	—

S_{BET} : BET specific surface area, S_{ex} : external surface area, V_p : primary mesopore volume, V_t : total pore volume, w_{BJH} : maximum of the pore size distribution calculated from the BJH method, WP, SC, SC_{ads} : weight percent, surface coverage calculated from the carbon contents, and surface coverage obtained from low pressure nitrogen adsorption, respectively, of the species introduced during the modification.

Quantities in brackets are calculated for 1 g of the MCM-41 material rather than 1 g of the modified sample.

*Estimated from the thermogravimetry.

of silica gels coated with CBPB (Kruk et al., 1997a) suggest that the amounts of CBPB in the samples currently studied are below the monolayer coverage. As can be seen from Table 1, the specific surface area, total pore volume and primary mesopore volume decreased significantly with the increase of the CBPB loading. However, the decrease in the primary mesopore size was very limited, which can be inferred from a rather small shift of the step of nitrogen condensation in primary mesopores (Fig. 1). To quantify the pore size changes, the BJH method was used. As can be seen in Fig. 2 and Table 1, even for the highest loading of CBPB (36%), the primary mesopore diameter decreased only by about 0.3 nm. This finding indicates that a limited amount of CBPB is actually deposited as a thin layer on the primary mesopore walls. Therefore, it may be inferred that CBPB is deposited on the external surface area of the sample or/and enters primary mesopores and blocks them. The conclusion about the limited surface coverage of CBPB on the pore walls is also supported by an examination of the adsorption isotherm (Fig. 1) and the pore size distribution (Fig. 2) of the chemically modified sample. Although the weight percent of trimethylsilyl groups was comparable to the weight percent of CBPB in the sample of the lowest coating level, the pore size decrease was more than 0.5 nm. The appearance of pore blocking is strongly supported by the fact that a significant decrease of the primary mesopore volume was observed for the coated samples, especially for the 36% CBPB MCM-41, which has the highest loading of CBPB (Table 1). Lower primary mesopore volumes for the coated materials are expected, since their pore sizes decreased and certain

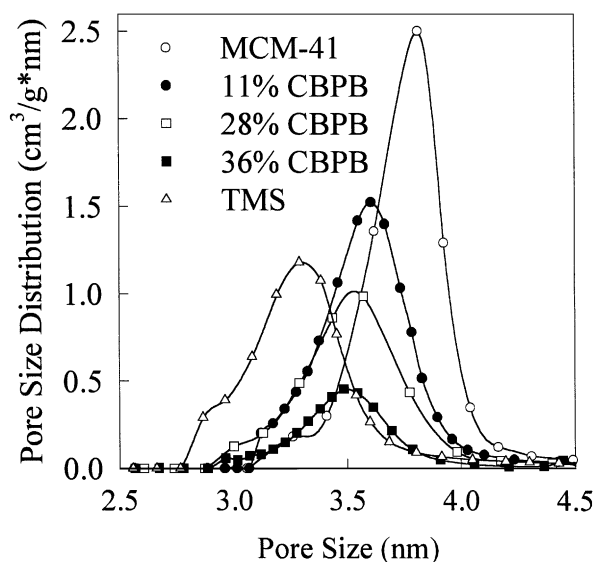


Figure 2. Pore size distributions for the samples (calculated from the BJH method with a modified Kelvin equation).

amounts of nonporous coating species were introduced. These two factors would lead to the following changes in the primary mesopore volume: $V_p, \text{ modified sample} = V_p, \text{ MCM-41} (1 - \% \text{CBPB}) \left(\frac{w_{\text{BJH, modified sample}}}{w_{\text{BJH, MCM-41}}} \right)^2$. The latter equation allows to predict V_p equal to 0.73, 0.58 and 0.49 cm³/g for materials with 11%, 28% and 36% CBPB, respectively. However, much lower primary mesopore volumes observed (0.64, 0.50 and 0.20 cm³/g, respectively). Such low values of V_p provide a direct evidence that some parts of primary mesopore structures of the coated MCM-41

materials are not accessible for nitrogen adsorbate, since the coating procedure is not expected to change the mesoporous structure of the support (i.e., siliceous MCM-41).

Changes in surface properties of the modified materials can be monitored using low pressure adsorption data to obtain high resolution α_s plots (Fig. 3) and the adsorption energy distributions (Fig. 4). One can notice

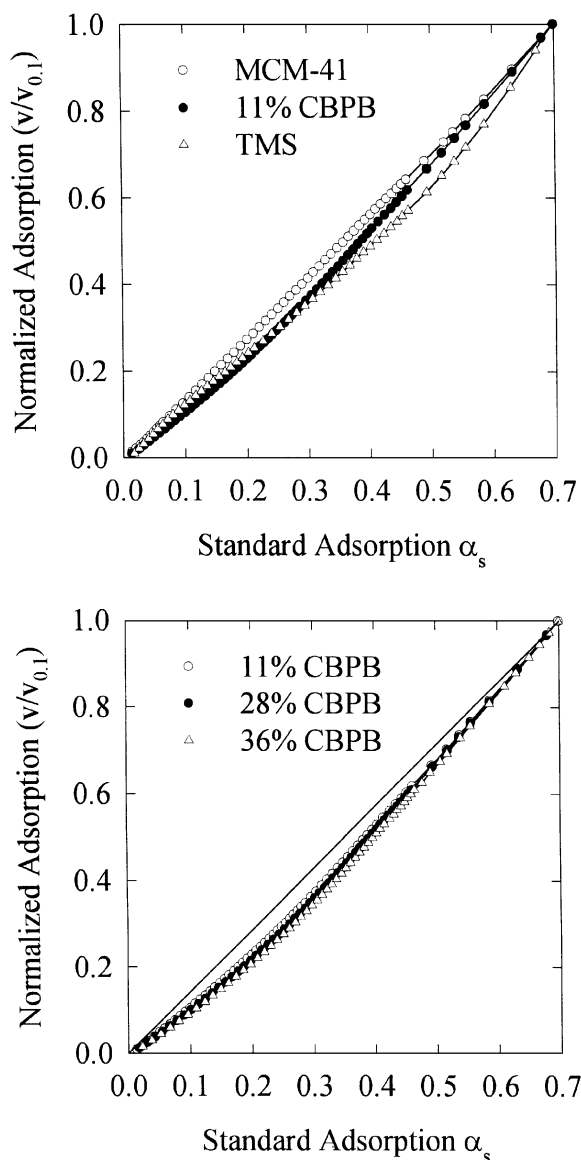


Figure 3. Low pressure parts of high resolution α_s -plots for the samples under study. To allow for a better comparison, the adsorbed amount was divided by the adsorbed amount at a relative pressure of 0.1. The line on the bottom graph was drawn to highlight the nonlinearity of the plots for the modified materials.

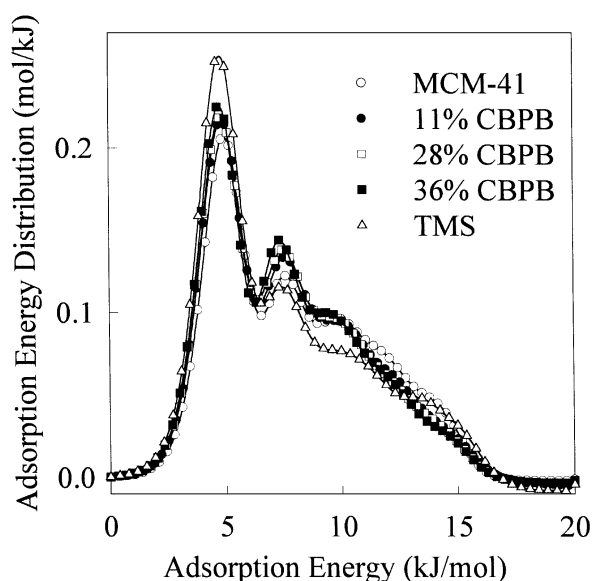


Figure 4. Adsorption energy distributions for the unmodified and the modified MCM-41 samples.

that when a macroporous silica gel is used as a reference, the low pressure part of the α_s -plot for the pure MCM-41 material is linear from the origin of the graph showing no trace of microporosity. In such a case, that initial part of the plot can be used to assess the total surface area of the sample (Sayari et al., 1997). In contrast, the low pressure segments of the α_s -plots for the modified samples show deviations from linearity, which is especially pronounced for the chemically modified material. The slope of the initial part of the plots increases with the increase in α_s (i.e., the plots are concave up), which is just opposite to the shape of comparative plot curves materials with micropores which are concave down (Gregg and Sing, 1982; Kaneko et al., 1992; Sayari et al., 1997). Such an unusual behavior can be attributed to the decrease in interactions between the surface and nitrogen molecules, caused by introduction of organic groups, which are much less polar than silanols present on the siliceous surface the MCM-41 (Kruk et al., 1997a; Jaroniec et al., 1997). Therefore, for the modified samples, an accurate assessment of the total surface area from the slope of the initial part of the α_s -plot is no longer practical, since proper reference materials would have to be used for different types of surface groups introduced and/or different surface coverages. However, one can use data in the multilayer adsorption region to assess the external surface area and primary mesopore volume, since the influence of the surface properties of materials is expected to be much

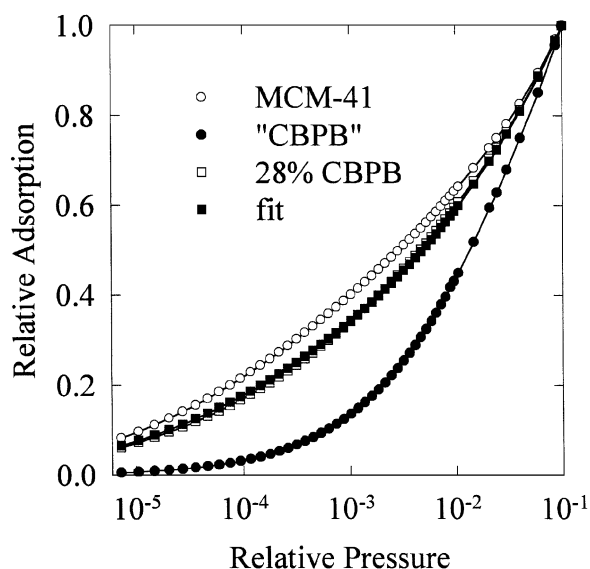


Figure 5. An illustrative fit of the relative adsorption curve for the 28% CBPB-MCM-41 by a linear combination of the relative adsorption curves for the unmodified MCM-41 and the sample of a silica gel with very high loading of chemically bonded and subsequently coated CBPB (the latter curve was assumed to correspond to adsorption on pure CBPB).

smaller for the multilayer formation (Gregg and Sing, 1982) than for adsorption in the submonolayer region.

As can be seen in Fig. 4, the adsorption energy distributions (AEDs) for the samples coated with CBPB resemble quite closely the AED for the unmodified MCM-41. The AED for TMS-MCM-41 is quite different from the others, since it has a noticeably lower population of adsorption sites at ca. 7–11 kJ/mol and higher population of low energy sites (ca. 5 kJ/mol). It should be noted that for the chemically modified sample, the high energy sites (about 14 kJ/mol), which can probably be attributed to isolated silanols (Kruk et al., 1997a; Jaroniec et al., 1997), are still significantly populated, which can be expected from a rather low degree of coverage of trimethylsilyl groups.

The fraction of the siliceous surface of coated materials, which was accessible to adsorbed molecules, was estimated by fitting low pressure relative adsorption curves of the modified samples with relative adsorption curves for the unmodified MCM-41 and the "CBPB". The adsorption isotherm for CBPB could not be measured directly due to low surface area and nonporous character of that substance. Therefore, it was approximated by the relative adsorption curve of the silica gel with high loading with chemically modified and coated CBPB, which was shown to be essentially fully covered

with CBPB (Kruk et al., 1997a). Note that the relative adsorption is defined here as the amount adsorbed at a given pressure divided by that for the relative pressure of 0.1. The fits were satisfactory and allowed to obtain the following estimates of fractions of the surface covered by CBPB: 0.18 (11% CBPB-MCM-41), 0.22 (28% CBPB-MCM-41) and 0.26 (36% CBPB-MCM-41). In order to assess the monolayer surface coverage of CBPB molecules, a similar fitting procedure was applied to the previously reported data (Kruk et al., 1997a) for the unmodified and CBPB-coated LiChrospher Si-100 silica gel. The results indicated that the monolayer of CBPB on the surface can be attained for the surface coverage less than or equal to $1.8 \mu\text{mol}/\text{m}^2$. Under such an assumption, the coverages SC_{ads} were calculated (see Table 1). SC_{ads} provides an estimate of the amount of CBPB molecules, which are present in the first layer on the surface of the MCM-41 materials (excluding the surface of pores blocked by CBPB, if such pores are present). Therefore, the comparison of SC_{ads} with the surface coverage SC (calculated from wt% CBPB) shows that CBPB actually covers a much smaller fraction of the surface than it would if it were distributed as a uniform layer. Therefore, it can be concluded that CBPB does not cover the surface in the uniform way, at least in the case of the two samples of the highest coating level (28% CBPB and 36% CBPB). Instead, it either enters primary mesopores and blocks them or accumulates at the external surface of the sample. Note that calculations of SC_{ads} may be quite inaccurate due to many assumptions involved.

Conclusions

Physical coating procedure did not allow to obtain a uniform surface coverage, probably due to a relatively large size of molecules used for the modification in comparison with the primary mesopore diameter. The chemical bonding led to significant changes of surface properties and the pore size of the MCM-41, showing the usefulness of that type of surface modifications. Nitrogen adsorption measurements proved to be an important tool to thoroughly characterize the modified materials.

Nomenclature

p	Equilibrium pressure	Pa
p_0	Saturation vapor pressure	Pa

R	The universal gas constant = 8.314	$\text{J mol}^{-1} \text{K}^{-1}$
r	Pore radius	nm
S_{BET}	BET specific surface area	m^2/g
SC	Surface coverage of species, calculated from the weight percent WC	$\mu\text{mol}/\text{m}^2$
SC_{ads}	Surface coverage of species, obtained from low pressure adsorption data	$\mu\text{mol}/\text{m}^2$
S_{ex}	External surface area	m^2/g
T	Absolute temperature	K
t	Statistical film thickness	nm
V_L	Molar volume of liquid nitrogen = 34.68	cm^3/mol
V_p	Primary mesopore volume	cm^3/g
V_t	Total pore volume	cm^3/g
w_{BJH}	Maximum of the pore size distribution calculated from the BJH method	nm
WP	Weight percent of species introduced during the modification	%
α_s	Standard reduced adsorption	
γ	Surface tension of liquid nitrogen at 77 K = 8.88×10^{-3}	N/m

References

- Barrett, E.P., L.G. Joyner, and P.P. Halenda, "The Determination of the Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms," *J. Am. Chem. Soc.*, **97**, 373–380 (1951).
- Beck, J.S., J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenker, "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates," *J. Am. Chem. Soc.*, **114**, 10834–10843 (1992).
- Brunel, D., A. Cauvel, F. Fajula, and F. DiRenzo, "MCM-41 Type Silicas as Supports for Immobilized Catalysts," *Zeolites: A Refined Tool for Designing Catalytic Sites*, L. Bonneviot and S. Kaliaguine (Eds.), pp. 173–180, Elsevier, Amsterdam, 1995.
- Feng, X., G.E. Fryxell, L.Q. Wang, A.Y. Kim, J. Liu, and K.M. Kemner, "Functionalized Monolayers on Ordered Mesoporous Supports," *Science*, **276**, 923–926 (1997).
- Gregg, S.J. and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
- Huo, Q., D.I. Margolese, and G.D. Stucky, "Surfactant Control of Phases in the Synthesis of Mesoporous Silica-Based Materials," *Chem. Mater.*, **8**, 1147–1160 (1996).
- Jaroniec, M. and R. Madey, *Physical Adsorption on Heterogeneous Surfaces*, Elsevier, Amsterdam, 1988.
- Jaroniec, C.P., R.K. Gilpin, and M. Jaroniec, "Adsorption and Thermogravimetric Studies of Silica-Based Amine Bonded Phases," *J. Phys. Chem. B*, **35**, 6861–6866 (1997).
- Kaneko, K., C. Ishii, M. Ruike, and H. Kuwabara, "Origin of Superhigh Surface Area and Microcrystalline Graphitic Structures of Activated Carbons," *Carbon*, **30**, 1075–1088 (1992).
- Khushalani D., A. Kuperman, G.A. Ozin, K. Tanaka, J. Garces, M.M. Olken, and N. Coombs, "Metamorphic Materials: Restructuring Siliceous Mesoporous Materials," *Adv. Mater.*, **7**, 842–846 (1995).
- Kruk, M., M. Jaroniec, R.K. Gilpin, and Y.W. Zhou, "Nitrogen Adsorption Studies of Coated and Chemically Modified Chromatographic Silica Gels," *Langmuir*, **13**, 545–550 (1997a).
- Kruk, M., M. Jaroniec, and A. Sayari, "Adsorption Study of Surface and Structural Properties of MCM-41 Materials of Different Pore Size," *J. Phys. Chem. B*, **101**, 583–589 (1997b).
- Kruk, M., M. Jaroniec, and A. Sayari, "Application of Large Pore MCM-41 Molecular Sieves to Improve Pore Size Analysis Using Nitrogen Adsorption Measurements," *Langmuir*, **13**, 6267–6273 (1997c).
- Rouquerol, J., D. Avnir, C.W. Fairbridge, D.H. Everett, J.H. Haynes, N. Pernicone, J.D.F. Ramsay, K.S.W. Sing, and K.K. Unger, "Recommendations for the Characterization of Porous Solids," *Pure Appl. Chem.*, **66**, 1739–1758 (1994).
- Ryoo, R. and S. Jun, "Improvement of Hydrothermal Stability of MCM-41 Using Salt Effects During Crystallization Process," *J. Phys. Chem. B*, **101**, 317–320 (1997).
- Sayari, A., "Catalysis by Crystalline Mesoporous Molecular Sieves," *Chem. Mater.*, **8**, 1840–1852 (1996a).
- Sayari, A., "Periodic Mesoporous Materials: Synthesis, Characterization and Potential Applications," *Recent Advances and New Horizons in Zeolite Science and Technology*, H. Chon, S.I. Woo, and S.-E. Park (Eds.), pp. 1–46, Elsevier, Amsterdam, 1996b.
- Sayari, A., P. Liu, M. Kruk, and M. Jaroniec, "Characterization of Large Pore MCM-41 Molecular Sieves Obtained via Hydrothermal Restructuring," *Chem. Mater.*, **9**, 2499–2506 (1997).
- Scott, R.P.W., *Silica Gel and Bonded Phases*, John Wiley & Sons, Chichester, 1993.
- Szombathely, M.V., M. Brauer, and M. Jaroniec, "The Solution of the Adsorption Integral Equations by Means of the Regularization Method," *J. Comput. Chem.*, **13**, 17–32 (1992).
- Vansant, E.F., P. Van der Voort, and K.C. Vrancken, *Characterization and Modification of the Silica Surface*, Elsevier, Amsterdam, 1995.
- Zhou, Y.W., M. Jaroniec, G.L. Hann, and R.K. Gilpin, "Gas Chromatographic and Infrared Studies of 4'-Cyano-4-biphenyl 4-(4-pentenyl)benzoate Coated on Porous Silica," *Anal. Chem.*, **66**, 1454–1458 (1994).