

Silylation of mesoporous silica MCM-41 with the mixture of $\text{Cl}(\text{CH}_2)_3\text{SiCl}_3$ and CH_3SiCl_3 : combination of adjustable grafting density and improved hydrothermal stability

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Abstract

Surface modification of MCM-41 with the mixture of $\text{Cl}(\text{CH}_2)_3\text{SiCl}_3$ and CH_3SiCl_3 produced chloropropyl–methyl-bifunctionalized MCM-41 in one pot. It was found that CH_3SiCl_3 as a small molecule silylating agent could be used as both a thinner to adjust chloropropyl group loading density and end-capping one to decrease the amount of silanol groups on mesoporous silica. The chloropropyl–methyl-bifunctionalized MCM-41 has a better hydrothermal stability than chloropropyl-functionalized MCM-41 due to improved surface hydrophobicity.

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1. Introduction

The discovery of mesoporous silica designated as MCM-41 by Mobil researchers has greatly expanded the possibilities for the design of new nano-structured materials [1]. Introduction of functional organic groups to the mesoporous silica via silylation is the most reliable method to design and prepare inorganic–organic hybrid materials, which enhance the functions of mesoporous silica in catalysis, separation and other new material field [2,3]. $\text{RSi}(\text{OEt})_3$ and RSiCl_3 are usually used as silylating agents. The former has a low activity, leading to relatively low loading and a large number of residual silanol groups after silylation [4,5]. The residual silanol groups after silylation on the surface, which are usually considered to lead to surface hydrophilicity [6] and may be influence seriously on catalytic activity [7,8], have to be end-capped with additional proce-

dures. Whereas, the latter has so high activity that free silanol and hydrogen-bonded silanol groups can react with it [9], probably resulting in high loading and difficulty in controlling its coverage with homogeneous distribution. In addition, for preparation of organically functionalized mesoporous materials, it is difficult to control the coverage of functional groups in wide range regardless of post-synthesis or co-condensation method [10].

Chloropropyl-functionalized MCM-41 is a key intermediate chosen by a lot of researchers to design and prepare other functionalized mesoporous materials [11,12]. In this work, $\text{Cl}(\text{CH}_2)_3\text{SiCl}_3$ and CH_3SiCl_3 as mixed silylating agents were firstly employed to silylate mesoporous silica MCM-41. As a result, both the hydrophobic methyl group and chloropropyl group as a reactive group were introduced onto mesoporous silica MCM-41 in one pot, producing chloropropyl–methyl-bifunctionalized MCM-41. It was found that CH_3SiCl_3 may be used as both a thinner, which can adjust or dilute the grafting density of chloropropyl group to obtain expected grafting density and an end-capping agent to decrease the amount of silanol groups on surface and improve hydrophobicity. The

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hydrothermal stability tests demonstrated that chloropropyl-methyl-bifunctionalized MCM-41 had better stability than chloropropyl-monofunctionalized MCM-41. Gas chromatography-atom emission detector (GC-AED), N_2 adsorption, XRD and solid state NMR techniques were employed to analyze the developed hybrid materials.

2. Materials and methods

2.1. Preparation of the materials

Mesoporous silica MCM-41 was prepared according to the reported procedure [13].

2.1.1. Silylation of MCM-41 with chloropropyltriethoxysilane

10.5 mmol of chloropropyltriethoxysilane with 0.3 ml of anhydrous pyridine or without pyridine was reacted with 3 g of MCM-41 (dried under vacuum at 200 °C for 8 h) dispersed in 60 ml dry toluene at toluene refluxing temperature for 16 h. The separated solid was extracted thoroughly in a Soxhlet apparatus with dry toluene and the mixture of diethylether and dichloromethane, then dried under vacuum at 150 °C for 8 h. Names of the resulting functionalized mesoporous silicas under different conditions were listed in Table 1.

2.1.2. Silylation of MCM-41 with chloropropyltrichlorosilane and methyltrichlorosilane

3.0 g of MCM-41 (dried under vacuum at 200 °C for 8 h) and 1.0 ml of anhydrous pyridine were added to 60 ml of dry toluene containing 10.5 mmol of chloropropyltrichlorosilane or methyltrichlorosilane under N_2 atmosphere. The reaction proceeded at 60 °C for 16 h, and then 4.0 ml of ethanol and 2.0 ml of anhydrous pyridine were added to the reacting system to make unreacted chlorosilane in solution convert to triethoxysilane and Si-Cl formed on surface convert to Si-OCH₂CH₃.

2.1.3. Silylation of MCM-41 with the mixture of chloropropyltrichlorosilane and methyltrichlorosilane

3.0 g of MCM-41 (dried under vacuum at 200 °C for 8 h) and 1.0 ml of anhydrous pyridine were added to 60 ml of dry toluene containing 10.5 mmol of a mixture of chloropropyltrichlorosilane and methyltrichlorosilane with fixed proportion. The remaining part of procedure was similar to silylation with chloropropyltrichlorosilane. When the molar ratio of chloropropyltrichlorosilane to methyltrichlorosilane was 0.6, the resulting material was named as MCM-41-cp-m(1). When the molar ratio of chloropropyltrichlorosilane to methyltrichlorosilane was 1.66, the corresponding material was denoted as MCM-41-cp-m(2).

2.2. Hydrothermal stability test

The hydrothermal test was performed according to Ref. [14]. 0.75 g of sample was dispersed in 60 ml of deionized water, and the mixed systems was heated in an autoclave at 95 °C for 18 h. After filtration and successively washings with water and ethanol, the sample was dried under vacuum. N_2 physical adsorption-desorption method was employed to evaluate the textural change after hydrothermal treatment.

2.3. Characterization and analysis

X-ray diffraction (XRD) patterns were recorded on Dmax-2500 (Rigaku); N_2 isotherms were obtained on ASAP2010 (micromeritics). Surface area was calculated from multipoint BET fit, and pore size distribution was calculated from adsorption branch using BJH method. Total pore volume was estimated at relative pressure of 0.99. ^{29}Si magic angle spinning NMR (^{29}Si MAS NMR) and ^{13}C cross-polarization magic angle spinning NMR (^{13}C CP MAS NMR) were performed on Infinity Plus 400 (Varian). For ^{29}Si MAS NMR, pulse width was 1.11 μs and pulse delay was 5.0 s, for ^{13}C CP MAS NMR, pulse width was 4.0 μs and pulse delay was 2.0 s. Unreacted chloropropylsilane and methylsilane were quantitatively analyzed with gas chromatography-atom emission detector (HP 6890GC-G2350A AED) through Cl and Si element channels. The grafting density of chloropropyl group was calculated from reacted chloropropyltrichlorosilane, and the total grafting density of chloropropyl and methyl group on bifunctionalized MCM-41 was calculated from reacted total silanes. The total grafting density subtracted the grafting density of chloropropyl group to obtain the grafting density of methyl group chloropropyltriethoxysilane (96%, GC) was used as a standard material.

Table 1
Sample names and synthesizing condition

Entry	Condition of silylation	Sample name
1	(EtO) ₃ Si(CH ₂) ₃ Cl, without pyridine	MCM-41-cp(1)
2	(EtO) ₃ Si(CH ₂) ₃ Cl, pyridine	MCM-41-cp(2)
3	Cl ₃ Si(CH ₂) ₃ Cl	MCM-41-cp(3)
4	Cl ₃ SiCH ₃	MCM-41-m
5	Cl ₃ Si(CH ₂) ₃ Cl, Cl ₃ SiCH ₃ (molar ratio is 3:5)	MCM-41-cp-m(1)
6	Cl ₃ Si(CH ₂) ₃ Cl, Cl ₃ SiCH ₃ (molar ratio is 5:3)	MCM-41-cp-m(2)

3. Results and discussion

3.1. Grafting density

Loadings of chloropropyl and methyl groups on various samples were summarized in Table 2. As one can see from Table 2, the total grafting density for the samples silylated with high active trichlorosilane agents is up to 1.48–1.90 mmol/g even at relatively low reaction temperature. Considering the result that the density of silanol group on mesoporous silica is between 2.5 and 3.0 per nm² [15], a conclusion may be drawn that a monolayer of organic groups formed on the surface of mesoporous silica and silanol groups were almost completely silylated. However, with alkoxy silane as silylating agent, the resulting coverage is relatively low even in the presence of pyridine as a base during the silylation process. As a result, the low loading was accompanied with a large amount of residual silanol groups on the surface [5], which has to be end-capped in order to obtain hydrophobic surface. The difference of loadings between chlorosilane and alkoxy silane also observed by other researchers is attributed to the difference in silylating activity mentioned in the introduction part [16]. It is noted that the coverage of methyl groups is higher than that of chloropropyl group from the comparison of MCM-41-m with MCM-41-cp(3), and the total grafting densities increase with increasing of methyl group coverage in the as-made bifunctionalized materials. This can be probably explained as Cl₃SiCH₃ with a small molecular size was limited by diffusion less than Cl₃Si(CH₂)₃Cl. It is the difference of molecular size that accounts for that the ratio of methyl group coverage to chloropropyl group coverage on the samples is higher than their initial molar composition before silylation. For MCM-41-cp-m(1), the ratio is 2.09, higher than the initial molar composition 1.66. For MCM-41-cp-m(2), the ratio is 0.82, higher than the initial molar composition 0.6. Although the ratio is not somewhat expected, it is reasonably believed that the chloropropyl group coverage is still adjusted in wide range through changing the composition of two chlorosilanes before silylation. CH₃SiCl₃ can be used as a

thinner to dilute other organic group coverage on the surface and favorably produce isolated catalytic active center.

3.2. N₂ physical adsorption–desorption and XRD characterization

N₂ physical adsorption–desorption is one of the most useful tools to characterize mesoporous materials. The isotherms of various samples and pore size distribution were shown in Figs. 1 and 2, respectively. The textural parameters of various samples were summarized in Table 3. For the isotherms, all the samples demonstrated typical mesoporous material type, i.e., IV type of isotherms, indicating that textural characteristics were not damaged during silylation. For the silylated samples,

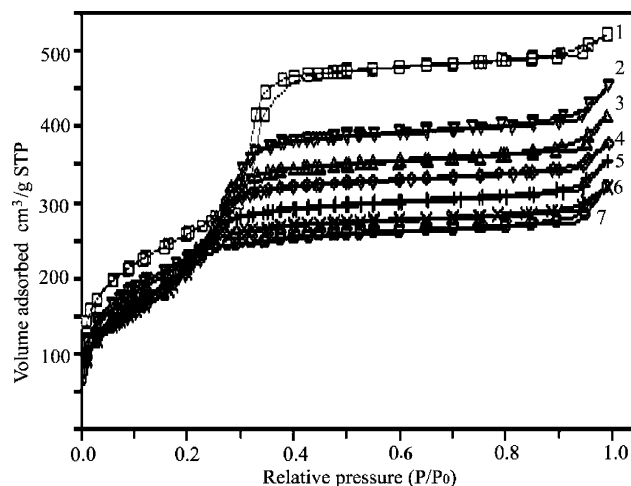


Fig. 1. Isotherms of MCM-41 and modified MCM-41: 1, MCM-41; 2, MCM-cp(1); 3, MCM-41(2); 4, MCM-41-m; 5, MCM-41-cp-m(1); 6, MCM-41-cp-m(2); 7, MCM-41-cp(3).

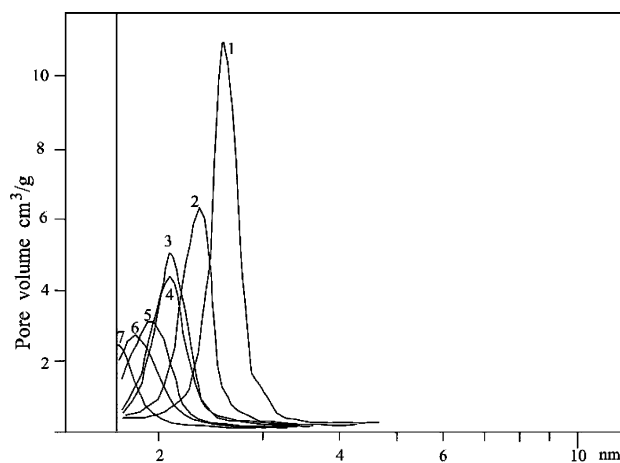


Fig. 2. Pore size distribution: 1, MCM-41; 2-MCM-cp(1); 3, MCM-41(2); 4, MCM-41-m; 5, MCM-41-cp-m(1); 6, MCM-41-cp-m(2); 7, MCM-41-cp(3).

Table 2
Loading of functional groups on MCM-41

Modified MCM-41	Chloropropyl group coverage, mmol/g	Methyl group coverage, mmol/g	Total coverage, mmol/g
MCM-41-cp(1)	0.72		0.72
MCM-41-cp(2)	0.95		0.95
MCM-41-cp(3)	1.48		1.48
MCM-41-m		1.90	1.90
MCM-41-cp-m(1)	0.56	1.17	1.73
MCM-41-cp-m(2)	0.88	0.72	1.60

Table 3
Textural parameters of functionalized MCM-41

Samples	Surface area <i>S</i> , m ² /g	Pore diameter <i>D</i> , nm	Pore volume <i>V</i> , cm ³ /g
MCM-41	903	2.7	0.82
MCM-41-cp(1)	777	2.4	0.69
MCM-41-cp(2)	745	2.1	0.61
MCM-41-m	698	2.1	0.59
MCM-41-cp-m(1)	687	1.9	0.55
MCM-41-cp-m(2)	663	1.8	0.50
MCM-41-cp(3)	615	1.7	0.49

Notes: *D*, the maximum pore size distribution by N₂ adsorption.

compared with the parent material MCM-41, the steep adsorption steps shifted to low pressure and the adsorption flat steps drop down. Pore size, surface area, and pore volume in Table 3 also decreased. This indicates the organic species were introduced into the channels. In Table 3, MCM-41-m with loading of 1.90 mmol/g still has a high surface area and big pore size, which demonstrates CH₃SiCl₃ with a small molecular size can be used as a thinner to dilute other functional organosilanes without drastically sacrificing of the surface and pore size. While, MCM-41-cp(3) with loading of 1.48 mmol/g has a relatively low surface and small pore size, which is not favorable to further modification. As expected, the pore sizes of MCM-41-cp-m(1) and MCM-41-cp-m(2) were between that of MCM-41-m and MCM-41-cp(3), and shift to low value with increasing of chloropropyl group loading. It is noted that these samples still have a large pore size, narrow pore size distribution, and a high surface area, which are favorable to further modification or functionalization.

XRD patterns of four samples were presented in Fig. 3. Modified MCM-41 still show the XRD patterns similar to the parent material MCM-41, which indicates the texture of initial material remained to some extent. However, the decrease in diffraction intensity and the absence of (110) and (200) reflections indicates that any structural order of the material did not extend over

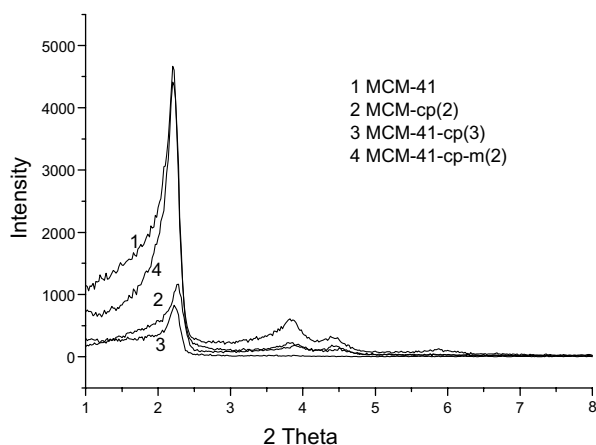


Fig. 3. XRD patterns of samples.

a long range, which is usually observed during modification of mesoporous materials [17].

3.3. Solid state NMR characterization

²⁹Si MAS NMR spectrum of chloropropyl-functionalized MCM-41 and chloropropyl-methyl-bifunctionalized MCM-41 were shown in Fig. 4 for comparison. The peak around 111 ppm is assigned to the Q₄ atom [(SiO)₄Si] of mesoporous silica. It is noted that there is a shoulder peak at 103.6 ppm in the ²⁹Si MAS NMR spectrum of MCM-41-cp, which is ascribed to the Q₃ environment [(SiO)₃SiOH], while this peak was not obviously observed in that of MCM-41-cp-m. This indicates that there were fewer silanol groups in MCM-41-cp-m and most of silanol groups were almost completely silylated due to introduction of trichloro-

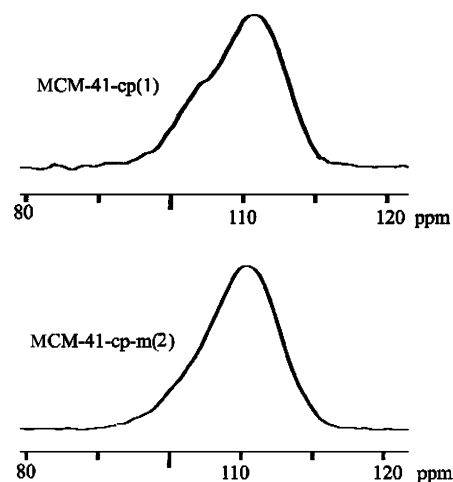


Fig. 4. ²⁹Si MAS NMR spectra of MCM-41-cp(1) and MCM-41-cp-m(1).

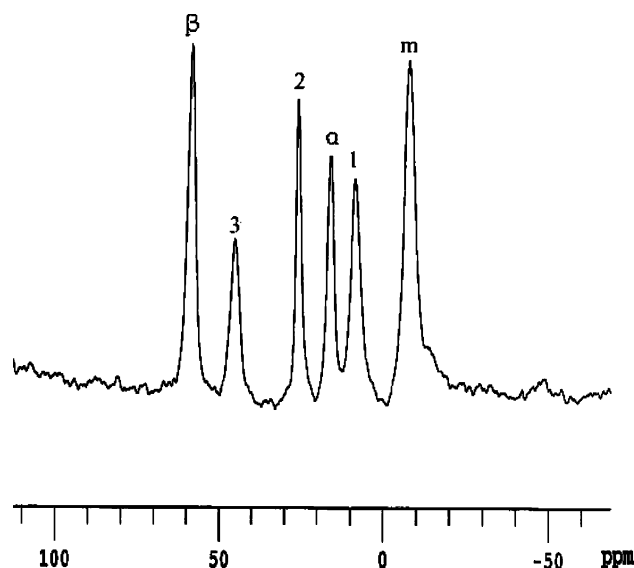
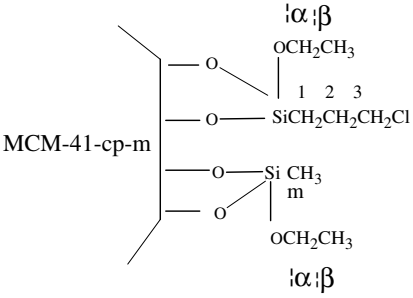


Fig. 5. ¹³C CP MAS NMR spectrum of MCM-41-cp-m(2).

Table 4
Chemical shifts

	Carbon	Chemical shift
	1	8.58
	2	25.83
	3	45.23
	α	15.94
	β	58.11
	m	-7.92

methylsilane. In addition, the ^{29}Si resonance peak observed around 60 ppm, which is ascribed to T environment $[(\text{SiO})_3\text{SiR}]$, indicates that organic groups were grafted on mesoporous silica via covalent bonds.

^{13}C CP MAS NMR spectrum of MCM-41-cp-m was shown in Fig. 5. Chemical shifts and assignments of various carbons on MCM-41-cp-m were summarized in Table 4. The simultaneous presence of peaks of carbons in chloropropyl group and methyl group suggest that these two groups were grafted on mesoporous silica through one-pot modification. Two peaks named as α and β appeared, indicating that Si-Cl unreacted with Si-OH on the mesoporous silica surface during silylation converted to Si-O-CH₂CH₃.

3.4. Hydrothermal stability of silylated MCM-41

The isotherms and pore size distribution of samples before or after being hydrothermally treated were presented in Figs. 6–10, and the textural parameters and their changes after hydrothermal treatment obtained by N₂ analyses were listed in Table 5. For unmodified MCM-41, the isotherm changed to III type from IV

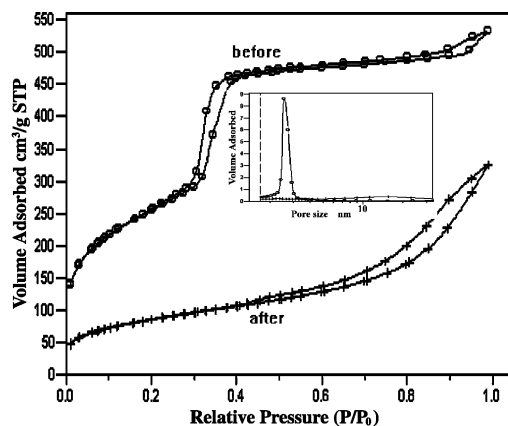


Fig. 6. Isotherms and pore distribution of MCM-41 hydrothermally treated before or after.

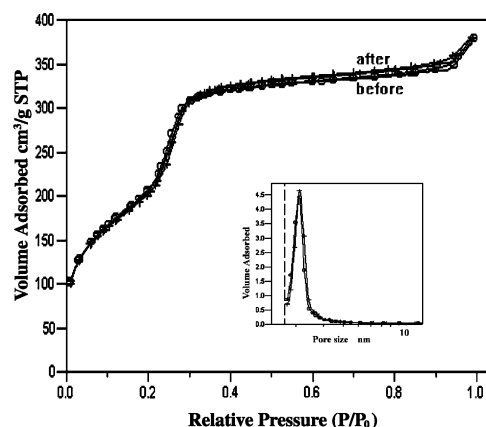


Fig. 7. Isotherms and pore distribution of MCM-41-m hydrothermally treated before or after.

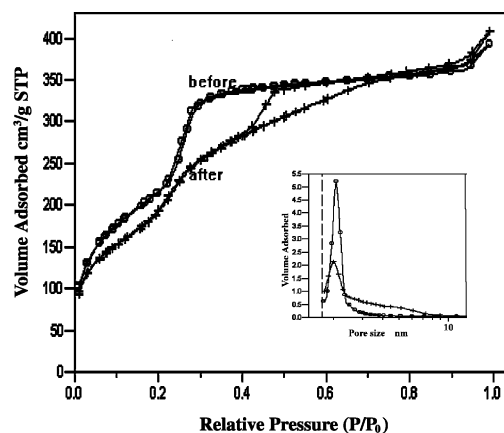


Fig. 8. Isotherms and pore distribution of MCM-41-cp hydrothermally treated before or after.

type, indicating the texture of unmodified MCM-41 was damaged seriously through hydrothermal treatment. As a result, surface and pore volume reduced drastically and pore size distribution was broadened. However, the isotherms of MCM-41 before and after silylation with Cl₃SiCH₃ are almost completely overlapped and

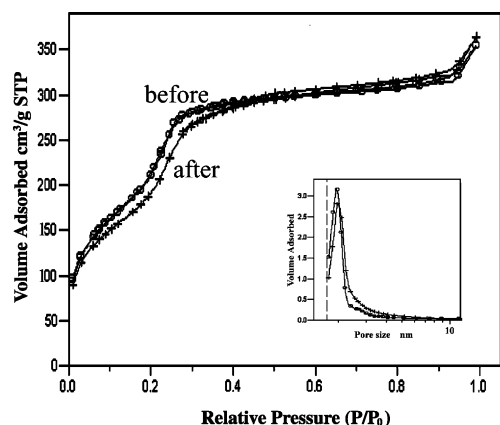


Fig. 9. Isotherms and pore distribution of MCM-41-cp-m(1) hydrothermally treated before or after.

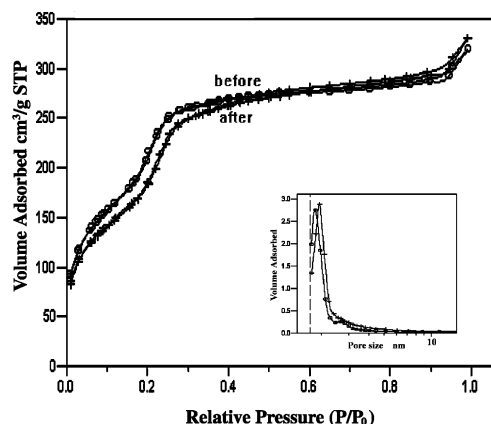


Fig. 10. Isotherms and pore distribution of MCM-41-cp-m(2) hydrothermally treated before or after.

Table 5

The textural changes of modified MCM-41 after hydrothermal treatment

Samples	Surface area		Pore volume		Pore size change after treatment
	S , m ² /g	ΔS	V , cm ³ /g	ΔV	
MCM-41	298	−605	0.50	−0.32	Increase
MCM-41-m	687	−12	0.50	0	No change
MCM-41-cp(2)	637	−108	0.63	+0.02	No change
MCM-41-cp-m(1)	631	−56	0.56	+0.01	Increase
MCM-41-cp-m(2)	618	−45	0.51	+0.01	Increase

textural parameters have no obvious change after hydrothermal treatment. These indicate silylation of MCM-41 with Cl_3SiCH_3 can remarkably improve its hydrothermal stability, which may be attributed that silanol groups were end-capped and the hydrophobicity of surface was enhanced. It is conceivable that water adsorbed onto silanol groups causes the hydrolysis of nearby Si–O–Si bonds, resulting in the collapse of the

ordered structure. The enhanced hydrophobicity of surface resulting from the decreased density of silanol group is favorable to hinder water to attack, and protect those Si–O–Si bonds from hydrolysis, resulting in a significant increase in hydrothermal stability.

For MCM-41-cp(2) after hydrothermal treatment, the isotherms have an apparent change. The steep adsorption step fade and a hysteresis loop appeared, which are indications of collapse of the ordered structure to some extent. As a result, the pore size distribution is broadened. However, for MCM-41-cp-m(1) and MCM-41-cp-m(2), the isotherms and pore distribution curves have only slight changes. Surface area decreased slightly, and pore volume and pore size were enlarged slightly. This may be interpreted that the framework of mesoporous silica was not instable and was enlarged during prolonged hydrothermal treating. The differences between MCM-41-cp-m and MCM-41-cp in process of hydrothermal treatment may be caused by changed surface properties including decreased coverage of Si–OH and enhanced hydrophobicity. The enhanced hydrophobicity probably facilitates organic molecules accessing to the surface and further modification. In addition, as a prospect, the silylation of mesoporous silica with the mixture of chlorosilane agents can lead to bifunctionalized material, which should be very useful in processes requiring controlled confinement or tailored surface, for example, where the channel reactivity needs to be coupled with the hydrophobic/ hydrophilic balance of the localized environment [18].

4. Conclusion

Chloropropyl–methyl-bifunctionalized MCM-41 was synthesized by one-pot surface modification with a mixture of $\text{Cl}_3\text{Si}(\text{CH}_2)_3\text{Cl}$ and Cl_3SiCH_3 . It was found that Cl_3SiCH_3 could be used as both a thinner to adjust chloropropyl group coverage through changing their adding proportion and an end-capping agents to eliminate silanol groups and improve surface hydrophobicity. The hydrothermal stability tests demonstrated chloropropyl–methyl-bifunctionalized MCM-41 had a better hydrothermal stability than chloropropyl-monofunctionalized MCM-41.

The developed strategy may be extended to preparing other bifunctionalized mesoporous materials. The surface hydrophobicity and channel chemical environment can be adjusted through changing the class of trichlorosilanes and their proportion.

Acknowledgements

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References

- [1] M.H. Lim, C.F. Blanford, A. Stein, *J. Am. Chem. Soc.* 119 (1997) 4090.
- [2] T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, *J. Am. Soc. Chem.* 125 (2003) 4688.
- [3] A.P. Wight, M.E. Davis, *Chem. Rev.* 102 (2002) 3589.
- [4] A. Cauvel, G. Renard, D. Brunel, *J. Org. Chem.* 62 (1997) 749.
- [5] P. Stutra, F. Fajula, D. Brunel, P. Lentz, G. Daelen, J.B. Nagy, *Colloids Surf. A* 158 (1999) 21.
- [6] S.G. Caravajal, D.E. Leyden, G.R. Quinting, G.E. Maciel, *Anal. Chem.* 60 (1988) 1776.
- [7] D. Brunel, N. Bellocq, P. Sutra, A. Cauvel, M. Laspéras, F.D. Renzo, A. Galarneau, F. Fajula, *Coord. Chem. Rev.* 178–180 (1998) 1085.
- [8] A.C. Blanc, D.J. Macquarrie, S. Valle, G. Renard, C.R. Quinn, D. Brunel, *Green Chem.* 2 (2000) 283.
- [9] C.G. Armistead, J.A. Hockey, *Trans. Faraday Soc.* 63 (1967) 2549.
- [10] M. Park, S. Komarneni, *Micropor. Mesopor. Mater.* 25 (1998) 75.
- [11] D. Brunel, *Micropor. Mesopor. Mater.* 27 (1999) 329.
- [12] C.E. Song, S.G. Lee, *Chem. Rev.* 102 (2002) 3495.
- [13] T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, *Nature* 402 (1999) 867.
- [14] B.H. Wouters, T. Chen, M. Dewilde, P.J. Grobet, *Micropor. Mesopor. Mater.* 44–45 (2001) 453.
- [15] X.S. Zhao, G.Q. Lu, A.K. Whittaker, G.J. Millar, H.Y. Zhu, *J. Phys. Chem. B* 101 (1997) 6525.
- [16] Y. Iwasawa, *Tailored Metal Catalysts*, D. Reidel Publishing Company, 1946, p. 25.
- [17] S. Zheng, L. Gao, J. Guo, *Mater. Chem. Phys.* 71 (2001) 174.
- [18] S.R. Hall, C.E. Fowler, B. Lebeau, S. Mann, *Chem. Commun.* 201 (1999) 201.