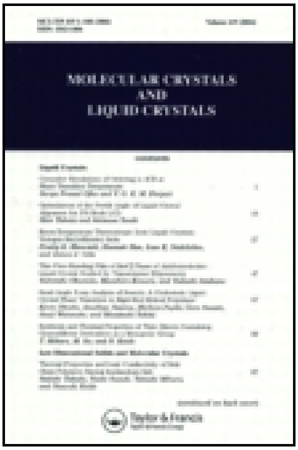
This article was downloaded by: [University of Haifa Library]
On: 20 August 2012, At: 10:55
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparation of Mesoporous Composite Materials by Pillaring of Magadiite with Silica

Ágnes Fudala [a] , Yoshimichi Kiyozumi [b] , Fujio Mizukami [b] , Makoto Toba [b] , Shu-Ichi Niwa [b] & Imre Kiricsp [a]

[a] Applied Chemistry Department, József Attila University, Szeged, H-6723

[b] NIMCR Surface Chemistry Department, Molecular Recognition Laboratory, 1-1 Highashi, Tsukuba, Iibaraki, 305, Japan

Version of record first published: 04 Oct 2006

To cite this article: Ágnes Fudala, Yoshimichi Kiyozumi, Fujio Mizukami, Makoto Toba, Shu-Ichi Niwa & Imre Kiricsp (1998): Preparation of Mesoporous Composite Materials by Pillaring of Magadiite with Silica, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 321-326

To link to this article: http://dx.doi.org/10.1080/10587259808042405

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 10:55 20 August 2012

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 321-326
Reprints available directly from the publisher
Photocopying permitted by license only

© 1998 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license
under the Gordon and Breach Science
Publishers imprint.
Printed in India.

Downloaded by [University of Haifa Library] at 10:55 20 August 2012

Preparation of Mesoporous Composite Materials by Pillaring of Magadiite with Silica

ÁGNES FUDALA[a], YOSHIMICHI KIYOZUMI[b], FUJIO MIZUKAMI[b], MAKOTO TOBA[b], SHU-ICHI NIWA[b], and IMRE KIRICSI[a]
[a]Applied Chemistry Department, József Attila University, Szeged, H-6723;
[b]NIMCR Surface Chemistry Department, Molecular Recognition Laboratory, 1-1 Highashi, Tsukuba, Iibaraki 305, Japan

Succesful attempt was made to intercalate silicate between the layers of sheet silicate magadiite. Both the interlayer distance and the BET value increased as the result of layers propped apart. SEM images evidence structure changes occured.

Keywords magadiite, intercalation, MCM-41, characterization

INTRODUCTION

Research activity devoted to the preparation of new mesoporous structures[1] include direct conversion of layered materials into porous metal silicates possessing micro- and mesoporous structure[2], direct synthesis of new materials of nanoscale pores[3], and intercalating various inorganic compounds inbetween the layers of sheet silicates to obtain materials of three dimensional framework.

Layered silicates, swollen with surfactant, can be transformed to a product similar to MCM-41[4]. The hexagonal arrangement of the channels is almost identical for both materials.

Nanotubes built up from various inorganic compounds such as carbon, TiO_2, V_2O_3 etc., have been synthesised[5].

Intercalation of organic and inorganic materials inbetween the layers of phyllosilicates such as smectites are well reported in the literature[6].

Intercalation of $PhSiCl_3$ or $C_6H_{11}SiCl_3$ between magadiite layers has been reported in 1990[7].

Keggin ions from partially hydrolized $AlCl_3$ solution has been deposited between the sheets of magadiite, resulting in a material $500m^2/g$ BET surface area[8].

For the first intercalation of silica into magadiite, tertaethyl orthosilicate (TEOS) gave a new material with $600m^2/g$ surface area was obtained[9].

In this work we report a new intercalation compound prepared by in situ synthesis of MCM-41 inbetween magadiite layers.

EXPERIMENTAL

Synthesis Procedures

Magadiite was hydrothermally synthesized by using the method of Schwieger *et al.*[10]. A mixture of $SiO_2:Na_2O:H_2O=9:1:75$ was heated at 403 K for 5 days. The white precipitate formed was carefully washed with double distilled water avoiding pH below 9.

For preparation of MCM-41 several procedures were tested. From the methods using various silica sources the procedure described by Ryoo *et al.* was selected[11], wich procedure starts from Ludox as silica source.

The synthesis of the silica intercalated magadiite was as follows. 20 g of hexadecyl-trimethylammonium chloride was mixed with 0.29 g of ammonia solution (28 wt%) at room temperature under vigorous stirring. Then 7.39 g of magadiite was added under continued stirring for 1 day. A gel was prepared by combining 46.9 g of 1 mol/dm^3 NaOH solution and 13.9 g of Ludox HS-40 (DuPont) under stirring for 2 h at 353 K. The detergent

Downloaded by [University of Haifa Library] at 10:55 20 August 2012

swollen magadiite was combined with this gel at room temperature. Stirring was continued for 1 day at 373 K. The pH of the solution was adjusted to 10.2 with acetic acid (30%) after the first, second and third days. After filtering, washing with distilled water, the material was dried at 373 K followed by calcination at 773 K for 10 h to burn the template off.

For comparision hexadecyl-trimethylammonium ion intercalated magadiite was also prepared.

Characterization

Samples were characterized by physical methods. XRD patterns were taken on powdered samples with a Russian made DRON 3 diffractometer. BET surface areas were measured in a volumetric equipment at 77 K. DTA-TG profiles were obtained using a Derivatograph-Q machine (Hungarian made) operating under computer control. SEM images were obtained using a Hitachi S-800 scanning electron microscope.

For IR characterization of the structural regions KBr pellet technique (1.5 mg sample in 100 mg KBr) was used. Spectra were run on a Mattson Genesis FTIR spectrometer. The spectra of OH groups were tested on self-supported wafers (thickness 10 mg/cm^2) pressed from the powdered materials and degassed at 623 K in the IR cell.

RESULTS AND DISCUSSION

The BET areas and interlayer distances are summarized in Table I. Data show that both the hexadecyl-trimethylammonium ions and the silicate in probable form of MCM-41 are intercalated between the sheets of magadiite. The interlayer distance for organic intercalated material (2.945 nm) is smaller compared to that of silicate intercalated structure (3.94 nm),

Downloaded by [University of Haifa Library] at 10:55 20 August 2012

Downloaded by [University of Haifa Library] at 10:55 20 August 2012

however these distances are much larger than that of magadiite (1.55 nm). BET areas increased from 38 m^2/g to 730 m^2/g as a result of intercalation of silicate inbetween the magadiite layers. Only slight increase in BET values was found for hexadecyl-trimethylammonium ion intercalated material.

TABLE I Physical characteristics of the prepared samples

Sample	As synthesied	Calcined form	
	XRD d_{100} [nm]	XRD d_{100} [nm]	BET [m^2/g]
MCM-41	3.944	3.944	773
Composite	4.016	3.841	730
HTA-magadiite	2.945	-	50
Magadiite	1.551	1.551	38

DTG profiles depicted in Fig. 1. indicate three weight loss steps for magadiite, four steps for intercalated material and the MCM-41. These weight losses should be due to release of water of various origins.

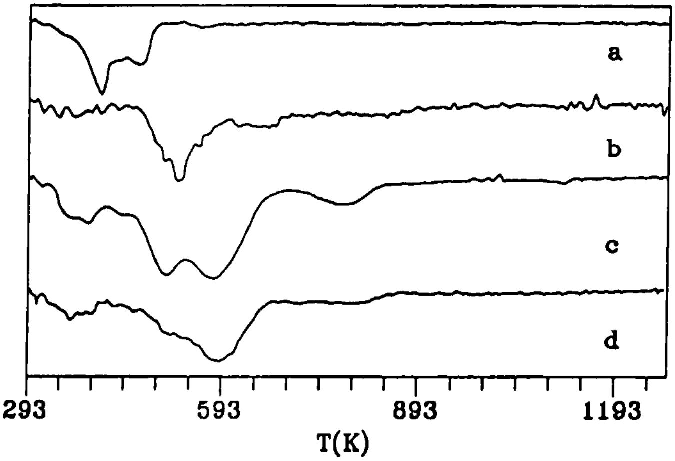


FIGURE 1. Derivatographic profiles of the as synhesied materials. (Magadiite (a), HTA-magadiite (b), composite (c), MCM-41 (d).)

Downloaded by [University of Haifa Library] at 10:55 20 August 2012

At around 400 K is the adsorbed water released and around 500 K water from partial dehydroxylation release. The step occuring at higher temperature is assumed to belong to the complete dehydroxylation leading to the formation of new Si-O-Si bonds for the expense of surface Si-OH groups.

By comparison of the SEM images, clear difference can be seen between magadiite, MCM-41 and the intercalated sample. Magadiite shows a layered, while MCM-41 a porous structure. On the picture of the silicate intercalated material both characteristics are to be seen. Unfortunately, the scanning electron mictroscopy give only rough information on the structural details.

IR spectra of materials in the range of OH vibrations are seen in Fig. 2. OH groups on the surface of magadiite, intercalated sample and MCM-41 absorb at 3660, 3740 and 3745 cm^{-1}, respectively. Each of these bands are due to the Si-OH groups since no other framework constituent is present in the samples. From this follows that these materials are weakly acidic if at al.

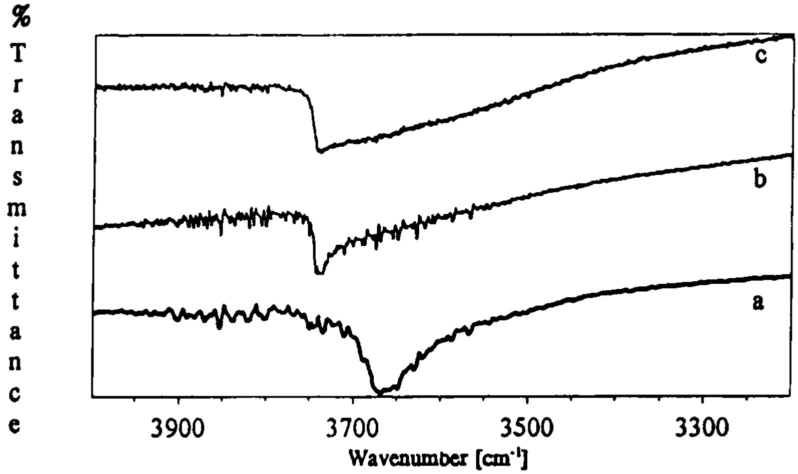


FIGURE 2. IR spectra of materials (pretreated in vacuum at 723 K) in the OH vibration range. (Magadiite (a), composite (b), MCM-41 (c)).

CONCLUSIONS

Silicate intercalated magadiite was synthesized and characterized by different methods. The sample thus prepared had a much larger surface area than the parent magadiite. This increase is due to the intercalation of high surface area silicate inbetween the layers.

The interlayer distance is bigger for the intercalated sample, which is also a result of the propping of the sheets of magadiite upon insertion of silicate.

The composite character of the new material is evidenced by the SEM images. The layered structure transforms to porous one other upon intercalation of silicate generated *in situ.*

The intercalated sample did not show acidic character by pyridine adsorption.

Downloaded by [University of Haifa Library] at 10:55 20 August 2012

REFERENCES

[1.] J.S. Beck, 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, *J. Am. Chem. Soc.*, **114**, 10834 (1992).

[2.] T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Japan,* **63**, 1535 (1990).

[3.] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J. C. Vartuli, J.S. Beck, *Nature,* **359,** 710 (1992)

[4.] T. Yanagisawa, K. Kuroda, C. Kato, *Bull. Chem. Soc. Japan,* **61**, 3743 (1988).

[5.] K. Hernadi, A. Fonesca, J.B. Nagy, D. Bernaerts, A. Lucas, *Carbon,* **34,** 1249 (1996).

[6.] F. Figureas, *Catal. Rev. Sci. Eng.*, **30,** 457 (1988).
R. Burch, *Catal. Today,* **2** (1988).

[7.] A. Galarneau, A. Barodawalla, T.J. Pinnavaia, *Nature,* **374,** 529 (1995).

[8.] S.-T. Wong, S. Cheng, *Chem. Mater.*, **5**, 770 (1993).

[9.] J.S. Dailey, T.J. Pinnavaia, *Chem. Mater.*, **4**, 855 (1992).

[10.] W. Schwieger, D. Heidemann, K.-H. Bergk, *Revue de Chimie Minerale,* **22**, 639 (1985).

[11.] J.M. Kim, J.H. Kwak, S. Jun, R. Ryoo, *J. Phys. Chem.*, **99,** 16742 (1995).