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Quantitative measurement of a mixture of mesophases cubic MCM-48 and hexagonal MCM-41 by 13C CP/MAS NMR

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Abstract

The ^{13}C CP/MAS NMR was used to quantify a mixture of cubic MCM-48 and hexagonal MCM-41 mesophases by means of interpretation of their surfactant organization, which cannot be determined by X-ray diffraction (XRD) techniques.
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Keywords: ^{13}C CP/MAS NMR; MCM-48; MCM-41; Characterization methods

1. Introduction

The determination of the percentages of two amorphous phases has always been of great importance in the understanding of properties of silicate materials, especially ordered mesoporous cubic MCM-48 and hexagonal MCM-41, which could be present in a mixture. MCM-48, with its highly interwoven and branched pore structure, is a potential adsorbent or catalyst support material in applications similar to which zeolites are now being used [1,2]. Because of the 3-D channel network of MCM-48, this material could have specific technological advantages. We report that by adjusting the concentration of NaOH during the synthesis a mixture of MCM-48 and MCM-41 is obtained. However, no single analytical technique is available to quantify the respective amount of MCM-48 and MCM-41 in the mixture. XRD is in general not particularly suitable for the quantitative phase composition determination for most ordered surfactant-templated materials, such as silica, because of noncrystallinity of their frameworks [3]. Here, we demonstrate that quantitative determination of mesophases is possible by interpretation of ^{13}C CP/MAS NMR spectra of a series of MCM-48 and MCM-41 mixtures.

2. Experimental

The synthesis of pure cubic MCM-48, pure hexagonal MCM-41 and mixed hexagonal-cubic phases were carried out via mixed cationic-neutral templating route using the cationic cetyltrimethylammonium bromide (CTABr) and neutral Triton X-100 (TX-100) surfactants. Rice husk ash (RHA), obtained from an open burning site was used as the silica source. In the first step, the sodium silicate was prepared by combining RHA (4 g, 93%SiO_2) with NaOH (1 g, Merck 99%) and H_2O (35 g). The mixture was then stirred for 2 h at 353 K. After that, this mixture was cooled to room temperature. The surfactant mixture was prepared by heating CTABr (3.87 g, Fluka, 99%) and TX-100 (1.17 g, Mallinckrodt, 97%) simultaneously in 55 g of H_2O. The surfactant solution was then cooled to room temperature. The sodium silicate solution and the surfactant solution were simultaneously poured into a 125 ml polypropylene bottle and shaken vigorously for 30 min. The gel mixture thus obtained was subsequently heated under static conditions at 370 K for 2 days in order to form the surfactant–silica mesophases. The pH of the mixture was then adjusted to 10.2. The reaction mixture was again heated for two more days following the pH adjustment. The molar composition of the final gel composition was $5SiO_2$:(1.00–2.00) Na_2O:0.15 TX-100:0.85 CTABr:400 H_2O. The amount of sodium hydroxide was varied in the range of 1.00 to 2.00 M. The precipitated product was filtered, washed with distilled water and dried in an oven at 370 K overnight. The samples

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were characterized by X-ray diffraction (XRD) analysis using D8 Bruker Diffractometer with a scanning range of 2Θ between $1.5°$ and $10°$ using copper $K\alpha$ ($\lambda =0.1542$ nm at 40 kV and 40 mA) as the source of radiation. The MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4 T spectrometer. The ^{13}C CP/MAS experiments were performed using a 3.8 μs $90°$ pulse with a delay time of 5 s, a contact time of 1 ms and spinning rate of 7 kHz and 2000 transients. Chemical shifts for ^{13}C were referred to TMS.

3. Results and discussion

Fig. 1 shows the diffraction patterns of mesophases MCM-48 and/or MCM-41 which were synthesized by adjusting the molar amount of NaOH from 1.0 to 2.0 M. With 1.25, 1.5 and 1.75 M concentration of NaOH, the low angle reflections between 2Θ values of $1.5°$ and $10°$ showed a change in intensities as the new, MCM-41 phase started to appear. The peaks at $2\Theta=3.8°$, $4.5°$ and $5.8°$ appear in sample (e) confirming that the sample was pure MCM-41, whereas the product pattern of sample (a) matched that of the pure MCM-48 phase. The low-angle peaks due to the silica matrix between 2Θ values of $1.5°$ and $10°$ clearly show that major peaks corresponding to the $Ia3d$ symmetry of the MCM-48 structure are observed in sample (a) [4,5]. Although the peaks at $2\Theta=3.8°$, $4.5°$ and $5.8°$ from the long-range ordering of mesophase MCM-41 are still clearly observed in the XRD pattern of sample (c), we cannot conclude that the sample is pure MCM-41, since the peaks at $2\Theta=1.6°$ and $2.7°$ for MCM-48 are overlapped by the XRD pattern of MCM-41. When samples (a) and (e) were mixed with a composition ratio of 50:50, the specific peaks for MCM-48 are no longer observed (Fig. 1f). This implies that in a mixture of hexagonal-cubic phase the presence of MCM-48 at a certain level could not be identified by XRD due to the very weak reflections.

Fig. 2 shows a series of the ^{31}C CP/MAS spectra; with increasing concentrations of NaOH. Interestingly, it is observed that the higher the intensity of C_5-C_{14} peak the higher the concentration of NaOH, suggesting that the organization of the surfactant is affected by the concentration of NaOH. The interaction of the surfactant and the MCM-48 caused considerable increase of the methylene chain (C_5-C_{14}) peak; which is not observed for MCM-41. This is acceptable due to the fact that the surfactant packing parameters g of MCM-48 and MCM-41 are different [6]. However, it should be noted that ^{13}C NMR peaks in MCM-41 mesophase are strongly dependent upon the contact time used for the ^{31}C CP/MAS NMR measurement [7]. In order to eliminate this possibility, in this work, all ^{13}C CP/MAS spectra were collected using the same contact time. Based on this phenomenon, the amount of MCM-48 and MCM-41 can be quantified by comparing the intensities of the C_5-
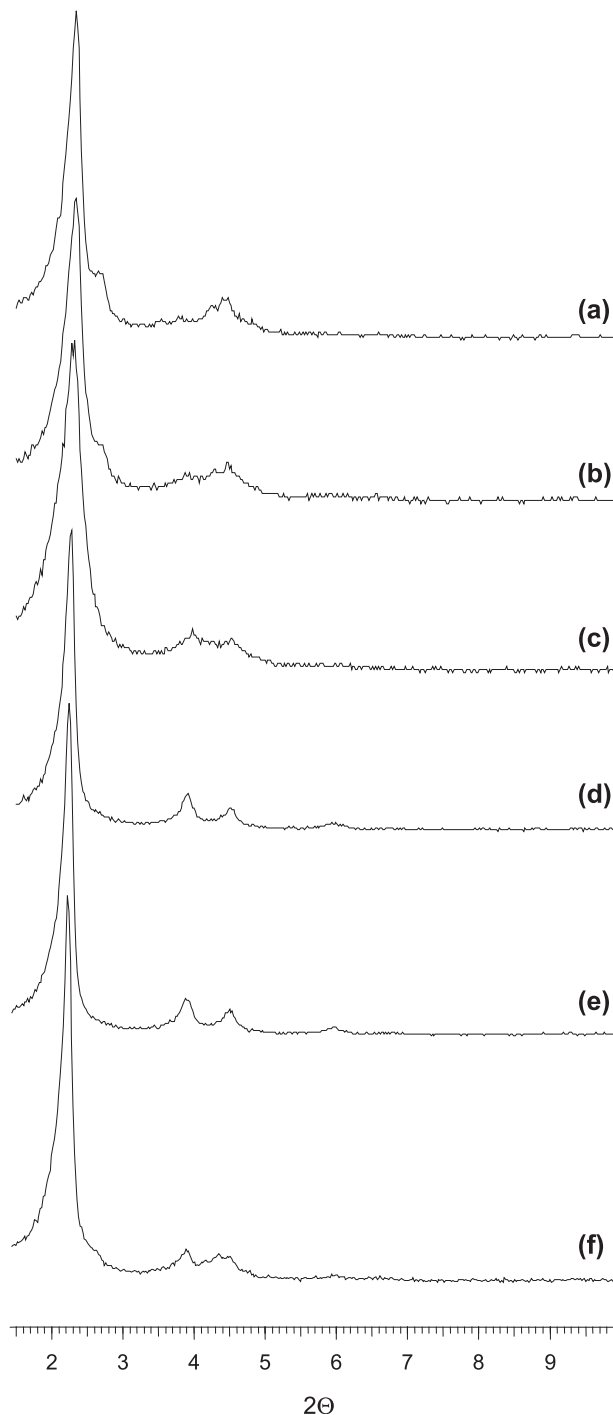

Fig. 1. X-ray diffraction (XRD) patterns of mesophases MCM-48 and/or MCM-41 prepared by difference of the NaOH concentrations; (a) 1.00 M, (b) 1.25 M, (c) 1.50 M, (d) 1.75 M and (e) 2.00 M. XRD pattern (f) was obtained by mixing samples (a) and (e) with the composition of 50:50.

C_{14} peaks. As shown in Fig. 3, the integrated intensity ratio of C_5-C_{14} and C_1 peaks is then normalized to the percentage of MCM-48 and MCM-41. A reasonably good correlation is obtained. This calculation was made with the assumption that the purity of samples (a) and (e) in Figs. 1 and 2 was 100%.
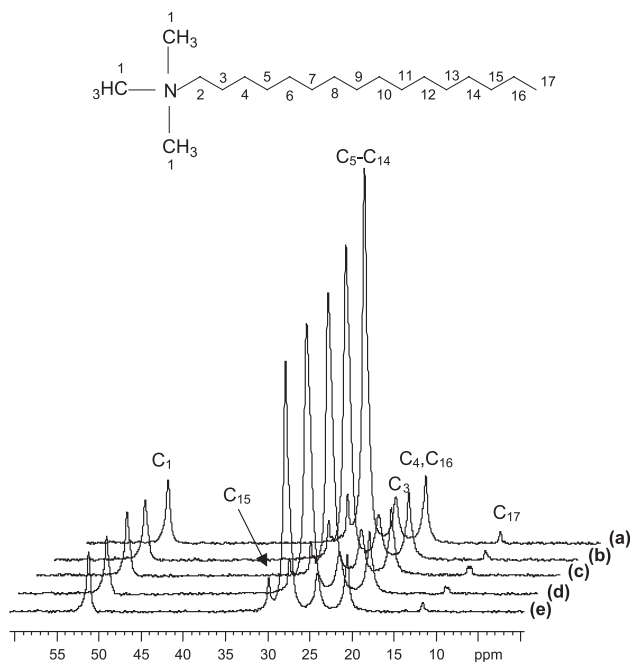
Fig. 2. ^{13}C CP/MAS spectra of mesophases MCM-48 and/or MCM-41 prepared with various NaOH concentrations; (a) 1.00 M, (b) 1.25 M, (c) 1.50 M, (d) 1.75 M and (e) 2.00 M. A contact time of 1 ms was applied.

Fig. 4. X-ray diffraction (XRD) patterns of mesoporous (a) MCM-48 and (b) MCM-41 after reinsertion of CTABr.

It is thought that the CTABr can be used as a probe molecule to determine the long-range order structure of mesoporous MCM-48 and MCM-41, after removal of template by calcination at 823 K for 6 h. It was observed that the BET surface area was ca. 1000 m^2 g^{-1}, and there was no significant difference in the shape of the nitrogen adsorption among the samples. The incorporation of CTABr into the pore of the samples was attempted by mixing the solid sample (0.1 g), CTABr (3.87 g) and H$_2$O (45 ml) at 373 K overnight and dried in an oven at 370 K. As shown in Fig. 4, after reinsertion of CTABr, the siliceous mesoporous samples partially collapsed after the hydrothermal treatment by surfactant solution. However, as analyzed by ^{13}C CP/
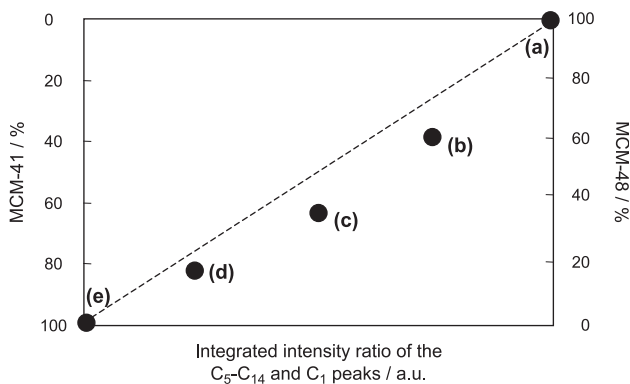
MAS NMR, as shown in Fig. 5, the intensities of the C$_5$–C$_{14}$ peaks of MCM-48 and MCM-41 are different. This suggests that the characteristic of a highly interwoven and branched pore structure of MCM-48 is still maintained after reinsertion of CTABr, although the sample was no longer well ordered.

This work has demonstrated that quantification of a mixture of cubic MCM-48 and hexagonal MCM-41 mesophases is possible by the interpretation of their ^{13}C CP/MAS NMR spectra, which cannot be determined by X-ray

Fig. 3. Integrated intensity ratio of the C$_5$–C$_{14}$ and C$_1$ peaks (normalized to percentage of mesophases MCM-48 and MCM-41), calculated from Fig. 2, of MCM-48 and/or MCM-41 prepared with various NaOH concentrations; (a) 1.00 M, (b) 1.25 M, (c) 1.50 M, (d) 1.75 M and (e) 2.00 M.
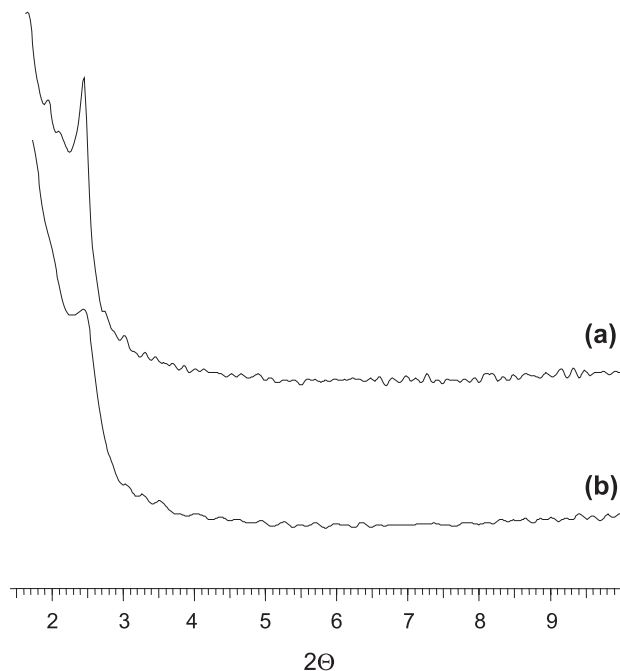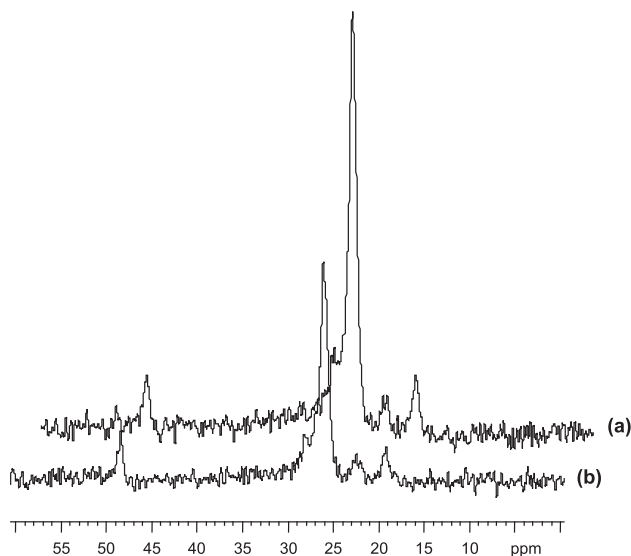

Fig. 5. ^{13}C CP/MAS spectra of mesoporous (a) MCM-48 and (b) MCM-41 after reinsertion of CTABr. A contact time of 1 ms was applied.

diffraction techniques. However, the availability of pure phases of MCM-48 and MCM-41 greatly facilitates the quantitative analysis. Although, at present, this method is only for semi-quantitative measurement of mesophase samples, we expect that this technique is applicable to a wide range of mesoporous structures. Further study on the improvement of the applicability of this technique using surfactant as a probe molecule in the determination of long-range order structure of mesoporous materials is now underway.

Acknowledgements

References

[1] C.T. Kresge, M.E. Leonowics, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowics, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[3] U. Ciesla, F. Schuth, Microporous Mesoporous Mater. 27 (1999) 131.
[4] A. Carlsson, M. Kaneda, Y. Sakamoto, O. Terasaki, R. Ryoo, S.H. Joo, J. Electron Microsc. 48 (1999) 795.
[5] R. Schmidt, M. Stöcker, D. Akporiaye, E.H. Tørstad, A. Olsen, Microporous Mater. 5 (1995) 1.
[6] J.C. Vartuli, K.D. Schmitt, C.T. Kresge, W.J. Roth, M.E. Leonowicz, S.B. McCullen, S.D. Hellring, J.S. Beck, J.L. Schlenker, D.H. Olson, E.W. Sheppard, Chem. Mater. 6 (1994) 2317.
[7] R. Simonutti, A. Comotti, S. Bracco, P. Sozzani, Chem. Mater. 13 (2001) 771.