

X-ray diffraction analysis of mesostructured materials by continuous density function technique

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A continuous density function technique has been developed for X-ray diffraction (XRD) structural investigations of mesostructured materials. The technique is designed for the analysis of the density distribution in materials exhibiting nanoscale (2-50 nm) ordering of structural elements without atomic long-range order. The results of structure investigations of a series of silicate, metallosilicate and carbon mesostructured materials with hexagonal and cubic symmetry are presented.

1. INTRODUCTION

The X-ray powder diffraction is one of the main methods applied to the characterization of mesostructured materials. However, apart from a number of studies published, this technique is mostly used for the qualitative ascription of materials to known structural types and for determining the lattice dimensions. The detailed analysis of mesostructures basing on the diffraction peak intensities still presents a challenge due to the severe disordering of these substances at atomic level. Recently, a novel XRD structure analysis method has been proposed and applied in the structural investigations of a series of two-dimensionally ordered mesoporous materials [1, 2]. Here we report further development of this technique for three-dimensionally ordered mesostructures and present the results of its application to the structure analysis of different materials, including MCM-41, SBA-15 (2-D hexagonal $p6mm$), MCM-48 (3-D cubic $Ia3d$) and carbon molecular sieves.

2. EXPERIMENTAL

X-ray powder diffraction data were collected on a laboratory diffractometer DRON-4 (Cu- $K\alpha$ radiation) and on a high-resolution diffractometer located in Siberian Center of Synchrotron Radiation.

The scheme of the continuous density function technique used for structural investigations is described as follows. The averaged density distribution in the material is modeled by

flexible analytical function ρ with adjustable parameters. The intensities of the diffraction reflections are calculated by the Fourier-transform of the model function. The adjustable parameters of ρ are refined by minimizing the difference between calculated and experimental powder diffraction profiles using the Rietveld technique [3]. The structure characteristics are determined from the refined model parameters. Additional unknown structure details can be revealed from the density distribution maps calculated by the inverse Fourier-transform based on the reflection intensities extracted from the powder diffraction profile and the initial phases derived from the refined model function.

The two-dimensional hexagonal mesostructures were modeled by the density distribution function proposed in [1]. To simulate the density distribution in cubic MCM-48 material and its carbon derivative CMK-1 [4] we designed a density function [5] based on the nodal approximation of the "Gyroid" periodic minimal surface [6]. The structural disorder was allowed for by the Debye-Waller factor.

3. RESULTS AND DISCUSSION

The application of the developed approach to the structure investigations of a series of mesoporous silicate, aluminosilicate, titanosilicate and carbon mesostructured materials allowed their comprehensive structural characterization. In Fig. 1 some results of structure modeling of three samples of MCM-41 silicate mesoporous material are presented. Sample 1 was synthesized at room temperature from an aqueous mixture of cetyltrimethylammonium bromide (CTAB), Ethanol, NH_3 and Tetraethoxysilane (TEOS). Sample 2 was obtained by heating sample 1 in the mother liquor for 2 hours at 383 K, and sample 3 was a calcined form of sample 2. The structure characteristics obtained for samples 1, 2, 3 are: unit cell – 4.37(1), 4.36(1), 4.26(1) nm; pore diameter – 3.67(4), 3.32(4), 3.32(4) nm; wall thickness – 0.70(4), 1.04(4), 0.94(4) nm; pore hexagonality – 67, 54, 37 %. As seen, the material formed at room temperature has the least wall thickness and the most hexagonal pores. After the thermal

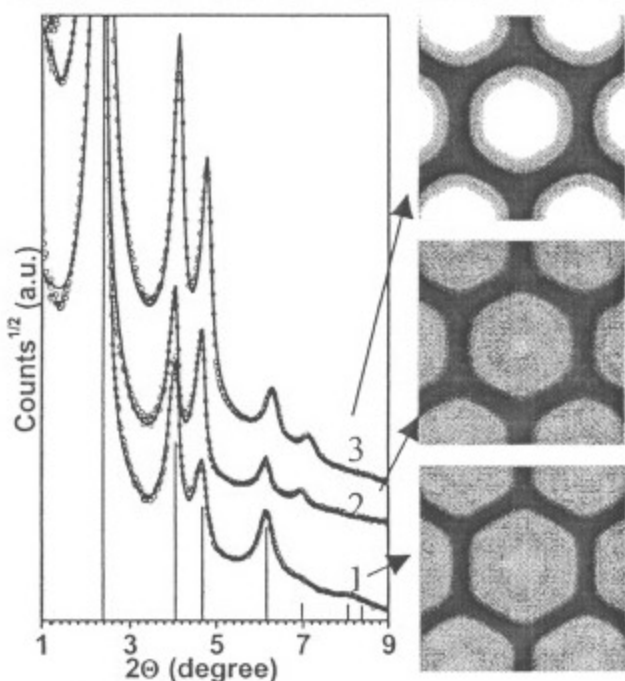


Fig. 1. Experimental (circles) and calculated (solid line) XRD powder patterns of three MCM-41 materials studied. Respective density distribution maps are shown.

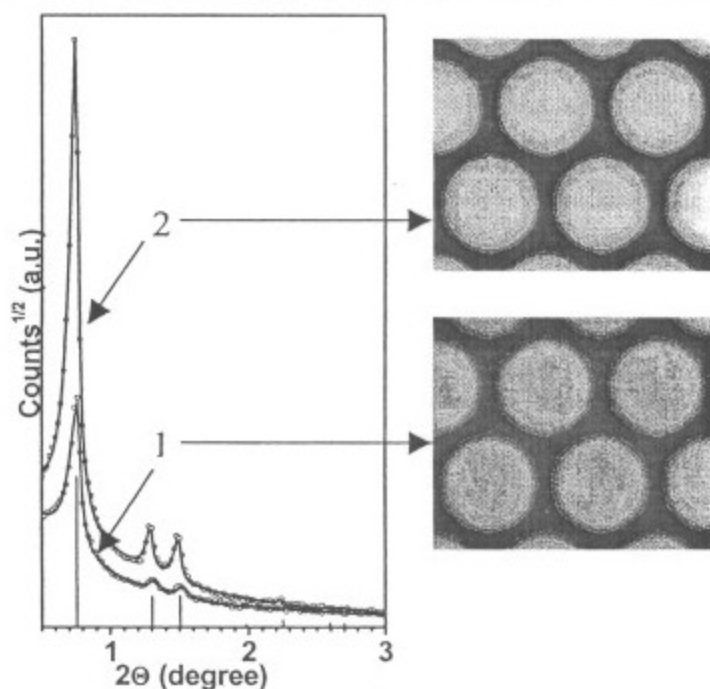


Fig. 2. Experimental and calculated XRD powder patterns of SBA-15 aluminosilicate at two stages of hydrothermal treatment and respective density distribution maps.

treatment in the mother liquor the wall thickened without unit cell expansion. The room temperature sample 1 was found to be unstable after calcination and boiling in water, but sample 3 was stable in boiling water and strong hydrochloric acid. We believe that this improvement of the material stability was due to the silica polycondensation and wall thickening without unit cell expansion. The surfactant distribution in the mesopores was found to be not uniform with distinct minimum in the pore centers. This feature was also observed in our previous studies [1, 2] for as-made silicate and metal-silicate MCM-41 materials obtained from different media.

In Fig. 2 the results of XRD structural studies of SBA-15 aluminosilicate mesoporous materials obtained at two stages of hydrothermal treatment are presented. The materials were synthesized in the presence of Pluronic 123 surfactant via hydrothermal treatment at 373 K for 16 (sample 1) and 48 (sample 2) hours. Both materials exhibited cylindrical mesopores of nearly the same diameter 9.85(5) nm and their unit cells were determined to be 13.39(3) and 13.66(2) nm respectively. The density distribution maps demonstrate the elution of surfactant from mesopores during the hydrothermal treatment. Our structural studies of different silicate and metal-silicate SBA-15 materials show that their pores are, basically, of less hexagonality than those of MCM-41 and the surfactant within the pores of SBA-15 is distributed more uniformly.

The structural studies of MCM-48 mesoporous material were carried out on samples synthesized by the well known procedure [7] from an aqueous mixture of CTAB, NaOH and TEOS at 383 K. The samples were highly ordered, exhibiting XRD reflections with d-spacing up to 1 nm. The results for the as-made form of the material are illustrated by Fig. 3. The refined structure model provided nearly perfect XRD profile fitting. The as-made and calcined materials were found to have the same wall thickness of 0.83(5) nm and unit cells of 9.57(1) and 9.00(1) nm respectively. The analysis of the Fourier density maps revealed that the distribution of surfactant in the pores of MCM-48 was not uniform (Fig. 3) with a central

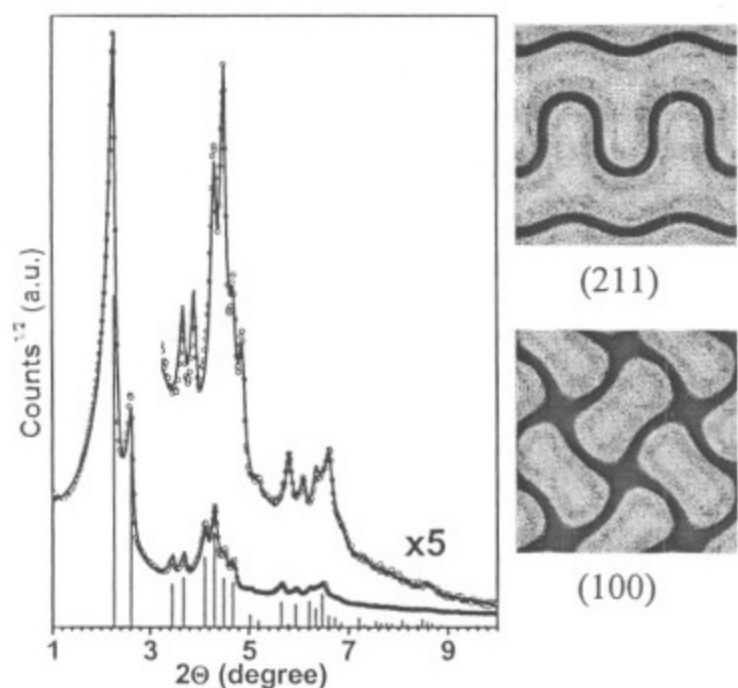


Fig. 3. Experimental (circles) and calculated (solid line) XRD powder patterns of as-made MCM-48. Sections (100) and (211) of the 3-D density distribution map are shown.

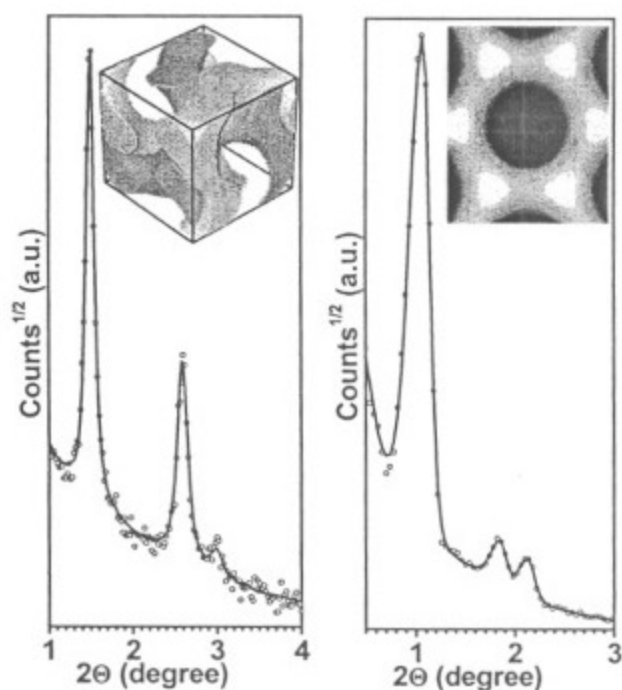


Fig. 4. XRD powder patterns and density distributions for CMK-1 (left) and CMK-3 (right) carbon molecular sieves.

