CHARACTERISTICS OF MOLECULAR SORPTION ON TEMPLATE CONTAINING MESOPOROUS MOLECULAR SIEVES OF TYPE MCM-41


Template containing materials of type MCM-41 have properties of microporous substances. On absorption into the micropores of such materials the dependence of the characteristic absorption energies on the molecular mass of the sorptive is extreme, and the specific absorption volume decreases with increased molar volume of the sorptive. A model is proposed to explain the peculiarities of the absorption properties of the template containing materials.

Self-aggregating mesoporous molecular sieves (MMS) of type MCM-41 undergo interactions with solutions of silicate anions and cations with a micellar structure to give equalization of charge density ("charge density matching") [1]. Subsequent condensation and formation of the silicate skeleton leads to a considerable decrease in the negative charge which may be accompanied by a weakening of the bonds of the surfactant in the silicate skeleton. As a result part of the surfactant may be washed out with water and a definite space, filled with water molecules, arises between the surface of the silicate skeleton and the micellar structure. It may be suggested that without any major disruption of the micellar structure a template containing MMS may possess some absorptive possibilities in consequence of the relatively small extent of condensation and lability of the silicate skeleton and also solubilization of the hydrophobic molecules of the surfactant micelles. The peculiarities of the sorption properties of such materials have not been studied previously.

It is known that the chromatographic separation of some substances is more effective at the surface of the sorbent of the stationary phase or the liquid crystalline phase when a surfactant molecule with long organic radicals is bonded to the surface of the carrier [2]. In this connection it appeared of interest to investigate the adsorptive properties of template containing MMS. In this work we have studied the sorption of water, alcohols, benzene, and n-hexane on three different MMS with the MCM-41 structure which were synthesized with quaternary ammonium salts with alkyl substituents of different lengths as surfactant templates: myristyltrimethylammonium bromide (C_{14}H_{29}N(CH₃)₃Br, MTMABr), cetyltrimethylammonium chloride (C_{16}H₃₃N(CH₃)₃Cl, CTMACl), and octadecyltrimethylammonium chloride (C_{18}H₃₇N(CH₃)₃Cl, ODTMACl) from Aldrich and Fluka.

Samples of MMS of type MCM-41 were obtained by a known method [1] from a reaction mixture of composition (mol): surfactant : sodium silicate : water = 0.35 : 1 : 400. To a solution of the surfactant a solution of sodium silicate was added with vigorous stirring, stirring was continued for 10 h and 3 M sulfuric acid was added to adjust the pH of the mixture to 9. The precipitate was filtered off after a day, washed with warm water and dried at 20 °C. Diffraction patterns of the samples were determined with a DRON-3M, CuKα.

Although the MMS with different templates were prepared under uniform conditions and with the same molar ratios of the reagents, their diffraction patterns of the samples were noticeably different (Fig. 1). On increasing the length of the alkyl radicals of the surfactant, the hexagonal structure in all cases was confirmed by the ratio of the Miller indexes (1 : 3 : 4 : 7) for MTMABr and CTMACl and (1 : 3) for ODTMACl (other small angle peaks were not resolved), but its perfection...
Fig. 1. Diffraction patterns of samples of type MCM-41 synthesized using MTMABr (a), CTMACI (b), and ODTMACI (c) as templates.

subsequently decreased. The reason for this effect of the length of the alkyl substituents may be connected in particular with differences in their solubility, the stereochemistry, and structure of the micelles. It will not be discussed here. The unit cell parameters \( (a_0 = 2d_{100}/\sqrt{3}) \) calculated for these samples were 44.3, 51.0, and 45.4 Å respectively.

Sorption isotherms of the vapors of the chosen substances by the template containing MMS were measured at 293 K after preliminary evacuation of the samples (residual pressure 0.1 Pa) for 3 h at 373 K. Analysis of the sorption isotherms was carried out using the equations of isotherms for the theory of volume filling of the micropores (TOZM) [3]:

\[
a = a_0 \exp \left[ -\left( \frac{E}{A} \right)^n \right],
\]

where \( a \) is the amount of sorption, mmol/g, \( a_0 \) is the limiting amount of sorption, mmol/g, \( E \) is the characteristic energy of absorption, kJ/mol, \( A \) is the differential molar work of absorption, kJ/mol, and \( n \) is the distribution range (equal to 1 in all of the cases studied of the absorption of substances on template containing MMS). The sorption isotherms in linear coordinates of this equation are given in Fig. 2.

For a satisfactory description of the sorption isotherms by the TOZM equation (Fig. 2) it follows that the template containing MMS are microporous substances. Sorption of comparatively small molecules (water, C\(_1\) and C\(_2\) alcohols) is basically by van der Waals interactions. This is indicated by the fact that the characteristic absorption energy \( E \) of these substances by the MMS increases, as in the case of a zeolite (silicalite, ZSM-5 structure) not containing active sorption centers [4, 5], symbatically with calculated increments of the Kveil parachor \( (\Pi) \) (erg\(^{1/4}\)-cm\(^{5/2}\)) of the sorptive (Table 1). In both cases the characteristic energy of absorption is close to 0.1\(\Pi \), as expected [7]. The somewhat higher values for the energy of sorption \( E \) of water, methanol, and ethanol on the MMS samples than for silicalite probably shows that the small dipolar molecules can freely interact with the charged head of the surfactant molecule and the hydrophilic centers of the surface of the silicate skeleton.