Influence of β-cyclodextrin on protolytic properties of MCM-41-type silica with immobilized aromatic amino groups

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In the present work, postsynthetic modification of external surface of MCM-41-type mesoporous silica particles (S_{sp}=1003 m^2/g, d_{pores}=2.42 nm) with aromatic amino groups was carried out. These groups can participate in the complexation with β-cyclodextrin (β-CD) forming surface pH-controlled nanovalves. Composition of grafted substances on the modified silica surfaces was confirmed by IR spectral and chemical analyses, and structural parameters of synthesized silicas were calculated from the data of x-ray diffraction and low-temperature adsorption-desorption of nitrogen.

It was found that immobilization of N-[N-(N-phenyl)-2-aminophenyl]-aminomethyl or N-[N-(N-phenyl)-2-aminophenyl]-3-aminopropyl groups on MCM-41 causes a decrease of the specific surface (839 and 782 m^2/g, respectively). At the same time, chemical modification does not affect the pore size, proving immobilization of functional groups only on the outer surface of particles.

Influence of β-CD on the protolytic properties of surface aromatic amino groups was studied by potentiometric titration method. It was proved that amino groups with different basicity exist in the system at an equimolar ratio of surface N-[N-(N-phenyl)-2-aminophenyl]-aminomethyl or N-[N-(N-phenyl)-2-aminophenyl]-3-aminopropyl groups and β-CD macromolecules supplied from a solution. In the surface layer of silicas there are free aromatic amino groups (pK_a = 4.66 and 4.83, respectively) and amino groups in the supramolecular complex with oligosaccharide (pK_a = 5.26 and 5.31, respectively). The increase in protonation constants of aromatic amino groups located on the external surface of silica particles is due to the formation of inclusion complexes with β-CD macromolecules. Hence, supramolecular structures formed near by entrances into the mesopores are able to control delivery of biologically active substances from pore volume of the carrier at pH change.