MESOPOROUS SILICA FUNCTIONALIZED WITH METHYL RED AS COLORIMETRIC pH SENSOR

Dziazko M. O., Roik N. V.
Chuiko Institute of Surface Chemistry of NAS of Ukraine, 17 General Naumov Str., Kyiv, 03164, Ukraine
dzyazko@ukr.net

Construction of pH sensors is widely studied for a variety of chemical, medical, and biochemical applications. One of the most reliable approaches to create pH sensing material with improved properties is immobilization of acid-base indicator on solid support. Among inorganic proton permeable carriers silica attracts considerable attention due to high chemical and thermal stability, good biocompatibility and optical transparency, negligible swelling in solvents, easy control on the structural parameters and chemical composition.

In the present work, we focused our attention on the synthesis of pH sensor based on mesoporous amorphous silica – silochrome C-120 with chemically immobilized methyl red (MR). On the first stage, aminopropyl silica was synthesized by the reaction between silanol groups of silica surface and ethoxy groups of (3-aminopropyl)triethoxysilane. Then, grafting of acid-base indicator MR on aminopropyl silica was realized under mild conditions by use of coupling agent (1,1′-carbonyldiimidazole).

The content of MR moieties chemically immobilized on silica support was estimated by chemical and thermogravimetric analysis of surface layer as well as using diffuse reflectance UV-Vis (DRUV) spectroscopy. In the case of chemical analysis, cleavage of grafted MR from the carrier was achieved by hydrolysis of amide bonds in aqueous medium and reaction solution was analyzed by transmittance UV-Vis spectroscopy. The results of thermogravimetric analysis obtained for silica carrier with grafted MR moieties were compared with that ones for aminopropyl silica and content of chemically immobilized dye was estimated from the difference in weight loss. To determine the amount of chemically bonded MR by DRUV spectroscopy, calibration curves plotted for a series of standards across a range of dye contents deposited on aminopropyl silica near its expected amounts in synthesized organosilicas were used. Obtained results are represented in Table. Comparison of the MR content estimated by chemical, thermogravimetric, and DRUV analysis proves good agreement of obtained results.

Table. Content of MR chemically immobilized on silica surface.

Silica	Content of MR		
	DRUV analysis, mmol/g	chemical analysis, mmol/g	thermogravimetric analysis, mmol/g
1-MR-NH_2-C-120	0.026	0.024	0.027
2-MR-NH_2-C-120	0.020	0.020	0.022
3-MR-NH_2-C-120	0.018	0.016	0.015

Chemical immobilization of MR on solid support may cause substantial changes in indicator's protolytic properties due to the involving of one of its functionalities into the covalent bonding with surface 3-aminopropyl groups. Therefore, acid-base equilibria of surface functional groups were studied by potentiometric titration method and the ionization constants values were estimated to confirm the ability of synthesized pH sensor material to acid-base response. It was found that the protonation of surface MR-containing functionalities proceeds at higher pH values in comparison with individual indicator dye.