

Politechnika Częstochowska  
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**Charakterystyka spektroskopowa i własności magnetyczne krzemionki mezoporowatej  
SBA-15 aktywowanej metalami**

**Spectroscopic characterization and magnetic properties of the SBA-15 mesoporous silica  
activated by metals**

praca doktorska

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## Abstract

The following dissertation is devoted to synthesis and characterization of SBA-15 silica containing metal ions anchored inside channels via propyl-phosphonate groups. The metals, used for activation of silica matrix, were: nickel, copper and iron.

The scientific object of the research shown in this thesis is mesoporous silica SBA-15 type. The SBA-15 was invented at The University of California in the year 1998. This unusually stable material is also non-toxic and its production is easy and low-cost. In pure form, SBA-15 has very limited application. Its potential applications results from the ease of functionalization. Currently, the synthesis of materials cannot be the purpose for its own sake. The synthesis route should be designed to obtain very precise molecules properties, that allow for specific application. The synthesis should be designed for obtaining nanotools. The SBA-15 mesoporous silica seems to be the ideal material for creating nanotools. Both inside pores as well as inside walls structure some molecules can be attached in order to provide some specific properties allowing for given application. It must be stressed that the key for obtaining the material with appropriate properties is homogenous distribution of active groups inside matrix, without any agglomerations. Only in this case there is a possibility of fine-tuning the distance between molecules therefore controlling of the material properties.

The main goal of the present thesis is a synthesis of the SBA-15 mesoporous silica containing homogeneously distributed active units and the in-depth investigation of the properties of obtained materials. The author applied recurrent procedure to obtain the ordered mesoporous silica with uniformly distributed active units. On the basis of obtained experimental results, the synthesis procedure has been optimized. In the thesis only the finally optimized synthesis procedure has been presented. Also the experimental results involve only the products, prepared according to the final synthesis route.

In order to obtain uniformly distributed active units, containing nickel, copper or iron, anchoring groups to attach the metal ions inside silica pores have been used. The propyl-phosphonate units have been applied. Moreover, to obtain the proper distribution of the anchoring groups, the co-condensation method has been applied as a base of synthesis route. The synthesis procedure has been described in details in the thesis.

The structural properties of obtained materials were examined under N<sub>2</sub> sorption analysis (BET and BJH), Transmission Electron Microscopy (TEM) and X-Ray diffraction. The BET analysis enabled the author to finding of specific surface area and pores diameter, while BJH showed pores sizes distribution. The structure of the obtained materials was directly observed by using TEM. The obtained micrographs showed, that perfectly hexagonal pores arrangement had been obtained. Estimation of pores size and walls thickness was also possible. The X-Ray spectroscopy confirmed the hexagonal pores arrangement.

The EDX analysis was regarded as a useful to confirm reaction between precursor groups and doping agent by showing the proportions between molar number of phosphorus and metal atoms. The EDX analysis was treated as a supporting investigation to confirm further analysis of the molecular structure.

The main method for testing molecular structure, in order to check the synthesis efficiency of the metal containing SBA-15 silica was Raman spectroscopy supported by numerical simulations. If the proposed probing route is used it is possible to concluded what molecular structure of silica-based functional materials are like in relatively easy and explicit way. The procedure applied here was based on the comparison of theoretical Raman spectra of the considered (tested) compound with reference molecule. On the basis of this juxtaposition, the author has been able to determine positions of characteristic Raman vibrational modes. These modes can be understood as Raman vibrations occurring only for one compound but are not present in others. It can be assumed, that characteristic Raman band cannot be overlapped by other vibrations, occurring for both molecules. Having

identified characteristic Raman vibrational modes it is possible to analyse experimental Raman spectra obtained both for the samples considered and reference ones. Considering the presence or absence of characteristic Raman modes, it is possible to conclude about the efficiency of synthesis procedure and the molecular structure of the sample. With the help of the characteristic modes method, the author has analysed the molecular structure of obtained materials.

Mössbauer spectroscopy has great usefulness as a tool for the study of structural and physical properties of numerous inorganic and organic materials, especially iron containing species. Mössbauer parameters give some valuable information about the state and environment of  $^{57}\text{Fe}$  ions. For this reason, this kind of research was applied for investigation of the iron-containing mesoporous silica. The application of the above mentioned spectroscopy is able to confirm bonding between the iron ions and phosphate groups (on the basis of differences between investigated samples and doping agent), thereby confirming the appropriate activation of the mesoporous silica SBA-15. In the thesis the results of Mössbauer spectroscopy have been shown and analysed. On the basis of comparative analysis of the spectra obtained for the investigated sample and pure doping agent, the author has established environments of iron ions in both samples.

The magnetic properties of the metal-containing SBA-15 silica samples were examined under SQUID magnetometry. On its base the author has been able to probe the efficiency of metal incorporation into the mesoporous silica and to test the response to the applied field of the magnetic moments of metal ions anchored to the SBA-15 matrix via propyl-phosphonate units. Interactions between metal-containing groups were also determined by using SQUID magnetometry.