Study of Bimetallic ZIF Structures for Adsorption Iodine and Chlorine by XANES

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Introduction
Zeolite imidazolate frameworks (ZIFs) have unique structural properties and unexpected thermal and chemical stability [1]. Widespread application of ZIFs is associated with gas sorption and storage, primarily due to a porous ZIFs structure. Recently was shown that ZIF-8 could be effectively used for a sorption of iodine, which is a volatile gaseous fission product [2]. Because elemental halogens play an important role in the industry, but they are toxic and volatile, it is an important research task to develop reliable methods for safe handling, storage, and transportation [3]. In this study we show application of bimetallic Zn$_{1-x}$Co$_x$C$_8$H$_{10}$N$_4$ ZIFs structures for sorption I$_2$ and Cl$_2$.

Experimental methods
In this study we synthesized Zn$_{1-x}$Co$_x$C$_8$H$_{10}$N$_4$ (x = 0.05, 0.25, 0.75) samples from zinc nitrate hexahydrate, cobalt nitrate hexahydrate and 2-methylimidazole by using microwave radiation as described in [4]. The crystal structure of Zn$_{1-x}$Co$_x$C$_8$H$_{10}$N$_4$ samples were characterized by means of powder X-ray diffraction (XRD) using Bruker D2 Phaser diffractometer (Cu k$_\alpha$, λ=1.5406 Å). The experimental Co K-edge (7709 eV) and Zn K-edge (9659 eV) XANES spectra were measured using in-house X-ray spectrometer Rigaku R-XAS Looper for samples before and after interaction with I$_2$ and Cl$_2$.

Results and discussion
The comparison of the XRD patterns for Zn$_{1-x}$Co$_x$C$_8$H$_{10}$N$_4$ samples before and after interaction with I$_2$ shows that the structure of samples does not changes. XANES absorption spectra of the Zn and Co K-edges for bimetallic Zn$_{1-x}$Co$_x$C$_8$H$_{10}$N$_4$ have no any shifts of white line due to changes in oxidation state of metallic atoms. The shape of spectra before and after interaction with I$_2$ is similar. This fact gives us opportunity to conclude that I$_2$ does not cause changes in ZIFs structure and sorbed into their pores. On the contrary, the XRD and XANES data for the Zn$_{1-x}$Co$_x$C$_8$H$_{10}$N$_4$ samples interacted with Cl$_2$ confirm the presence of the structural changes. This may be caused by the bond formation between chlorine atoms and linkers in the ZIF structure.

Conclusions
In present work the bimetallic ZIFs Zn$_{1-x}$Co$_x$C$_8$H$_{10}$N$_4$ (x = 0.05, 0.25, 0.75) samples were synthesized. Using XRD and XANES techniques the structure of Zn$_{1-x}$Co$_x$C$_8$H$_{10}$N$_4$ samples before and after interaction with volatile I$_2$ and Cl$_2$ were studied.
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References