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Yulia Podkovyrina[1], Vera Butova[1], Elena Bulanova[1], Andriy Budnyk[1], Maria Kremennaya[1], Alexander Soldatov[1], Carlo Lamberti[1,2,3]

[1] The Smart Materials Research Center, Southern Federal University, Sladkova 178/24, 344090, Rostov-on-Don, Russia
[2] Department of Chemistry, INSTM Reference Center and CrisDi interdepartmental Center for crystallography University of Turin, via Giuria, I-10125, Torino, Italy
[3] Department of Physics and NIS interdepartmental Center, University of Torino, via Giuria 1, I-10125, Torino, Italy

E-mail: podkovyrina@sfedu.ru

Abstract. The local atomic structure in bimetallic Co/Zn zeolitic imidazolate frameworks (ZIFs) was studied using X-ray Absorption Fine Structure (XAFS) spectroscopy and theoretical calculations. The experimental Co K-edge and Zn K-edge XANES (X-ray Absorption Near Edge Structure) spectra of $Zn_{1-x}Co_xC_8H_{10}N_4$ samples (x = 0.05, 0.25, 0.75) synthesized by microwave synthesis were compared with the data for the ZIF-67 (x=1) and ZIF-8 (x=0). Theoretical XANES spectra for the bimetallic ZIFs were calculated. It was shown that in bimetallic ZIFs the Co and Zn atoms have the similar local environment.

1. Introduction

Unique structural properties, such as high porosity, surface area, and unexpected thermal and chemical stability of ZIFs are successfully applied in catalysis, gas separation and storage [1, 2]. ZIF-8 is expected to be effectively applied for adsorption of iodine isotopes which are a by-product of nuclear fuel cycle [3]. Most ZIF structures having been studied over the last years are based on a single metal. The fabrication of bimetallic ZIFs, however, is very likely to open up an opportunity for introducing new unique properties in ZIFs which could be efficient for a number of applications. This implies the necessity to thoroughly investigate the local environment of metal centers in heteroatomic ZIFs.

This work focusess on research into the local atomic structure of $Zn_{1-x}Co_xC_8H_{10}N_4$ materials by applying the XANES technique, due to its sensitivity to changes in the local environment of absorbing atoms [4-6].

2. Synthesis and Characterization

In this study we synthesized $Zn_{1-x}Co_xC_8H_{10}N_4$ (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 [7]. ZIF-8 (x = 0) and ZIF-67 (x = 1) were synthesized analogously using respective metal salts. The resulting solutions were heated in a microwave oven (MARS 6) for 120 min at 140° C. Then the obtained powders were collected by centrifugation, washed several times with methanol and dried at 60°. The crystal structure of $Zn_{1-x}Co_xC_8H_{10}N_4$ samples were characterized by means of powder X-ray

diffraction (XRD) using Bruker D2 Phaser diffractometer (Cu k_α, 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.

3. Results and discussion

The XRD patterns of the synthesized $Zn_{1-x}Co_xC_8H_{10}N_4$ samples display sharp and prominent peaks analogous to those of ZIF-8 and ZIF-67 presented in Figure 1. This suggests that the bimetallic ZIFs have the same crystalline structure as that of ZIF-8. Elemental mapping through scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) presented in Figure 2 shows that Co and Zn atoms are uniformly distributed in the $Zn_{0.5}Co_{0.5}C_8H_{10}N_4$ sample. The experimental XANES spectra of Co K-edge and Zn K-edge were measured for $Zn_{1-x}Co_xC_8H_{10}N_4$ samples (Figure 3). They are identical to the absorption spectra for the ZIF-8 and ZIF-67, which allows us to conclude that the local environment around Zn and Co atoms in the structure of bimetallic ZIFs is identical to the structure of monometallic ZIFs. Consequently, cobalt ions occupy partially zinc positions with tetrahedral coordination. This allows us to assume that oxidation state of cobalt ions is +2 due to their tetrahedral coordination, which is not the case with Co^{3+} ions.

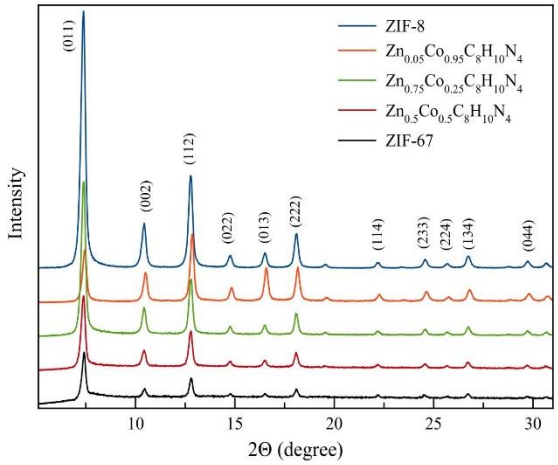

Figure 1. XRD data for bimetallic $Zn_{1-x}Co_xC_8H_{10}N_4$ samples (x = 0.05, 0.25, 0.5), ZIF-8 and ZIF-67

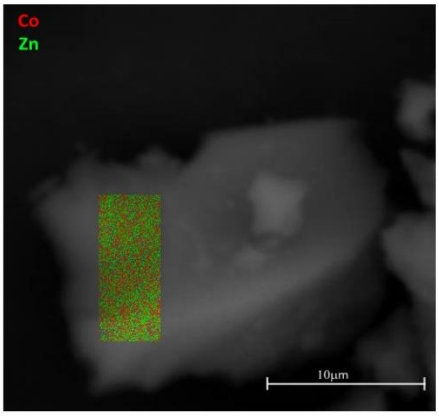

Figure2. SEM-EDS mapping for $Zn_{0.5}Co_{0.5}C_8H_{10}N_4$

A well-resolved pre-edge feature in Co K-edge XANES spectra (~7,700 eV) is characterized by an 1s→3d electronic transition. In accordance with the selection rule ($\Delta l = \pm 1$), such an electronic transition is forbidden in centrosymmetric compounds having octahedral environment around absorbing atoms.

Thus, the pre-edge feature on the XANES spectra of the Co-ZIF-67 and $Zn_{1-x}Co_xC_8H_{10}N_4$ materials clearly indicates that the local environment of cobalt atoms is not centrally symmetric and confirms the tetrahedral symmetry. The position of the absorption edge and the white line (~ 7708 eV) on the XANES spectra for the ZIF-67 (x=1) sample and the bimetallic $Zn_{1-x}Co_xC_8H_{10}N_4$ samples coincide, which means that the bimetallic ZIFs as well as the original Co-based ZIF-67 material contain divalent cobalt ions.

To prove that the local environment of the metallic atoms in ZIF-8 and ZIF-67 does not change after adding another metal to the structure, the theoretical spectra (Figure 4) were calculated using the finite difference method implemented in FDMNES [8] software. The calculations were performed for atomic clusters of 6 Å around the metal atom (Co or Zn). To simulate the XANES spectra we used crystallographic data for ZIF-8 and ZIF-67 from the Crystallography Open Database [9, 10]. It should be noted that theoretical spectra have some spectral features that are not seen in the experimental spectra, being the result of experimental resolution (1.9 eV for Co K-edge and 4.1 eV for Zn K-edge).

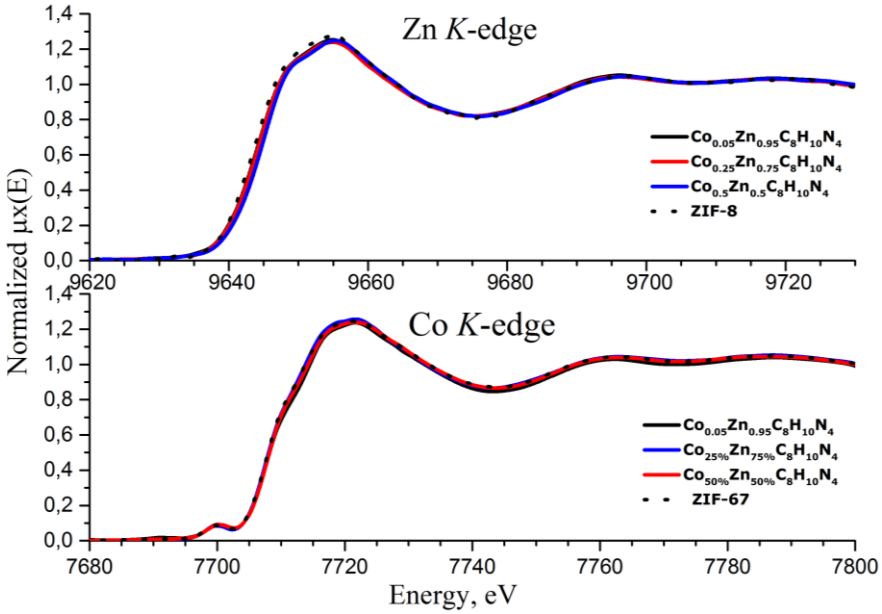

Figure 3. The experimental Co *K*-edge and Zn *K*-edge XANES spectra of $Zn_{1-x}Co_xC_8H_{10}N_4$ samples compared with ZIF-8 and ZIF-67

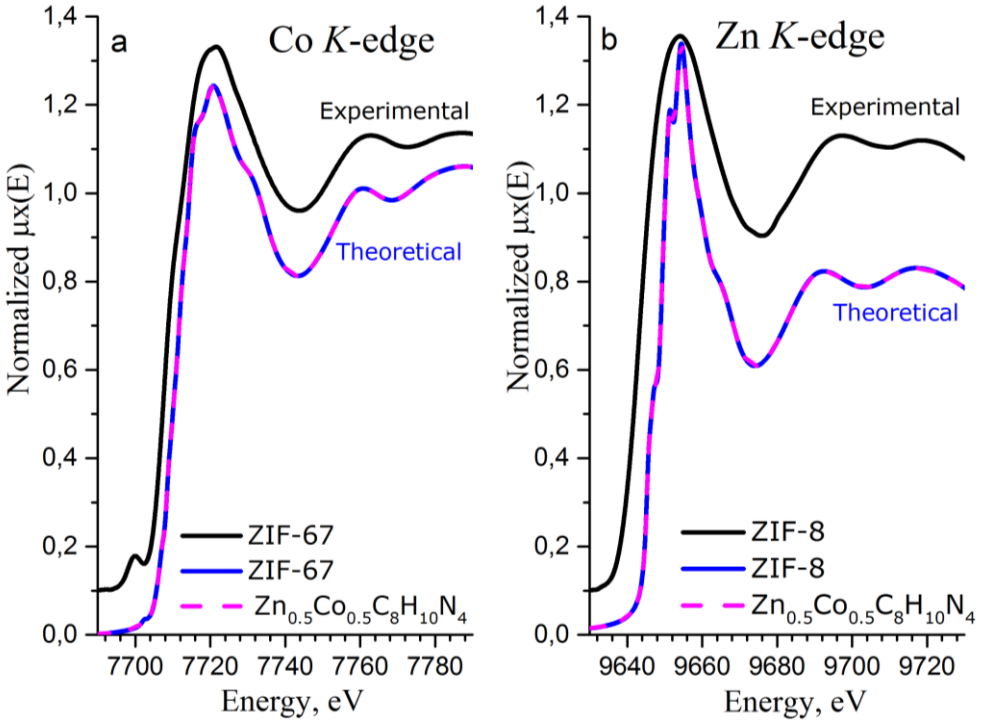

Figure 4. Comparison of the experimental and theoretical Co *K*-edge (a) and Zn *K*-edge (b) XANES spectra for ZIF-67 and ZIF-8 with theoretical spectra for bimetallic $Zn_{0.5}Co_{0.5}C_8H_{10}N_4$

To calculate the XANES spectra for bimetallic $Zn_{0.5}Co_{0.5}C_8H_{10}N_4$, we used the crystallographic data available for ZIF-67 and ZIF-8, and replaced the Co or Zn atoms in the nearest environment of the absorbing atom in the ratio 50/50. We found that the theoretical spectra for the monometallic ZIF-8 and ZIF-67 structures and bimetallic $Zn_{0.5}Co_{0.5}C_8H_{10}N_4$ were virtually identical.

4. Conclusions

XRD patterns of synthesized $Zn_{1-x}Co_xC_8H_{10}N_4$ samples (x = 0.05, 0.25, 0.75) displayed sharp and prominent peaks analogous to those of ZIF-8 suggesting that the bimetallic ZIFs have the same crystalline structure. The XANES absorption spectra of the Zn and Co K-edges for bimetallic Zn1-xCoxC8H10N4 samples were found to be identical to the absorption spectra for the pure ZIF-8 and ZIF-67, which allows us to conclude that the local atomic structure around Zn and Co atoms in the structure of bimetallic ZIFs is identical to the structure of monometallic ZIFs.

Acknowledgements

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