

Accepted Manuscript

Research paper

The effect of cobalt content in Zn/Co-ZIF-8 on iodine capping properties

Vera V. Butova, Elena A. Bulanova, Vladimir A. Polyakov, Alexander A. Guda, Abdelaziz M. Aboraia, Shapovalov V. Viktor, Heba Y. Zahran, Ibrahim S. Yahia, Alexander V. Soldatov

PII: S0020-1693(19)30142-2
DOI: <https://doi.org/10.1016/j.ica.2019.04.011>
Reference: ICA 18856

To appear in: *Inorganica Chimica Acta*

Received Date: 21 January 2019
Revised Date: 5 April 2019
Accepted Date: 5 April 2019

Please cite this article as: V.V. Butova, E.A. Bulanova, V.A. Polyakov, A.A. Guda, A.M. Aboraia, S.V. Viktor, H.Y. Zahran, I.S. Yahia, A.V. Soldatov, The effect of cobalt content in Zn/Co-ZIF-8 on iodine capping properties, *Inorganica Chimica Acta* (2019), doi: <https://doi.org/10.1016/j.ica.2019.04.011>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



The effect of cobalt content in Zn/Co-ZIF-8 on iodine capping properties

Vera V. Butova^{1,2}, Elena A. Bulanova¹, Vladimir A. Polyakov¹, Alexander A. Guda¹, Abdelaziz M. Aboraia^{1,3}, Shapovalov V. Viktor¹, Heba Y. Zahran^{4,5}, Ibrahim S. Yahia^{4,5}, Alexander V. Soldatov¹

¹ *The Smart Materials Research Institute, Southern Federal University, 5 Zorge Street, Rostov-on-Don, 344090, Russia*

² *Federal Research Centre the Southern Scientific Center of the Russian Academy of Sciences, Rostov-on-Don, Russia*

³ *Department of Physics, Faculty of Science, Al-Azhar University, 71542 Assiut, Egypt*

⁴ *Advanced Functional Materials & Optoelectronic Laboratory (AFMOL), Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia.*

⁵ *Metallurgical Lab., Nanoscience Laboratory for Environmental and Bio-medical Applications (NLEBA), Semiconductor Lab., Physics Department, Faculty of Education, Ain Shams University, Roxy, 11757 Cairo, Egypt.*

Abstract

We have tested for iodine sorption properties a variety of samples with ZIF-8 structure and various Zn/Co ratios (100/0, 95/5, 75/25, 50/50 and 0/100 in mol%). For iodine saturation, an excess of sublimated iodine crystals was used. We have observed that the prevailing trend for all compositions is adsorption of most of the iodine molecules by the internal surface and retaining them up to framework collapse. However, Co-doping results in a small decrease in the thermal stability of the samples after iodine saturation. Moreover, in the samples with high cobalt content, the part of iodine adsorbed by the external surface is higher than in zinc analogs. Combination of TGA and FTIR data evaluated the impact of lower flexibility of Co-linker bonds on the transfer of iodine molecules from the external surface of the crystals to internal pores.

Introduction

Nuclear power plant accidents and nuclear weapon tests lead to the contamination of the environment by two radioactive iodine isotopes – ¹³¹I and ¹²⁹I [1-3]. Both iodine isotopes are absorbed by the body and preferentially concentrated in the thyroid. As radionuclides decay, they may cause diseases associated with prolonged irradiation of the body from within, like thyroid cancer [4, 5] (see SI Section 1, Fig.S1). From this point of view, iodine capping is of paramount importance. For this aim, different materials were tested. Part of them is based on the physical sorption of the iodine gas by porous materials, and another one is based on chemical interaction between iodine molecules and the surface of the sorbent (see SI Section 2) [6-12]. However, these materials have some disadvantages, like a low temperature of iodine release, high cost, and low environmental friendliness.

Metal-organic frameworks (MOFs) are a rather new class of porous materials with high specific surface area (SSA) and a great variety of possible functional groups in the structure and pore geometry and size [13-18]. In this way, MOFs could be applied for iodine sorption. A variety of MOFs was already tested for this application [19-26]. Some examples are provided in SI Table S1. Two main points for a successful iodine decontamination are high iodine uptake and a high temperature of iodine release. One of the best candidates for iodine sorption is ZIF-8. It is constructed from Zn²⁺ ions tetrahedrally coordinated by nitrogen atoms from imidazole rings of linkers – 2-methylimidazole (MIm) (Fig S2). ZIF-8 demonstrates both high iodine uptake and a high temperature of iodine release [27]. The ZIF-8 framework strongly binds I₂ molecules due to an ideal geometry of the ZIF-8 pores: it allows to form two iodine–organic bonds per each I₂

molecule while traditional iodine–organic complexes are restrained to iodine located on the surface of ZIF-8. The small windows between pores combined with a strong I₂-framework-binding leads to a retention of I₂ up to framework collapse [28].

In the present work, we have investigated the effects of the metal sites composition on the iodine sorption properties. For this aim, we have replaced zinc ions in ZIF-8 with cobalt ions. So, we have tested for iodine sorption two mono-metal ZIFs – ZIF-8 and ZIF-67 and for the first-time three bimetallic ZIFs, containing both metals in the structure in various ratios. It allowed us to observe important trends caused by the metal sites composition.

Experimental section

All initial samples were obtained by slightly adopted MW assisted synthesis technique (Section 4 in SI) [29, 30]. In brief, a DMF solution of 2-methylimidazole (MIm) was mixed with a DMF solution of Zn(NO₃)₂ or/and Co(NO₃)₂, and TEA was added dropwise. The resulting mixture was placed into a hermetically sealed glass vessel and heated in a MW oven for 15 minutes at 140 °C. After cooling down, the precipitate was separated using centrifugation, washed three times with DMF. All molar ratios and sample designations are provided in Table 1.

Table 1 Molar ratios of the initial substances, used for the synthesis of ZIFs.

Sample designation	Formula	Molar ratio				
		Zn ²⁺	Co ²⁺	MIm	TEA	DMF
ZIF-8	ZnC ₈ H ₁₀ N ₄	1	-	4	2.6	289
95Zn5Co	Zn _{0.95} Co _{0.05} C ₈ H ₁₀ N ₄	0.95	0.05	4	2.6	289
75Zn25Co	Zn _{0.75} Co _{0.25} C ₈ H ₁₀ N ₄	0.75	0.25	4	2.6	289
50Zn50Co	Zn _{0.50} Co _{0.50} C ₈ H ₁₀ N ₄	0.50	0.50	4	2.6	289
ZIF-67	CoC ₈ H ₁₀ N ₄	-	1	4	2.6	289

For the iodine sorption experiments, the respective sample was pressed into a thin tablet and activated for at least 4 hours at 200 °C. After this, the tablet on a metallic stand was placed into a glass vessel with iodine crystals, closed with a glass cap and heated up to 110 °C (SI Fig. S4). After complete iodine sublimation, a sample was held in this atmosphere for one hour. Then the vessel was opened, and excess of the iodine gas was evacuated. Obtained samples are designated as ZIF-8+I₂, 95Zn5Co+I₂, 75Zn25Co+I₂, 50Zn50Co+I₂, ZIF-67+I₂. Part of each sample was additionally heated at 250 °C for 2 hours in air. In this way we have obtained 5 more samples: ZIF-8+I₂+T, 95Zn5Co+I₂+T, 75Zn25Co+I₂+T, 50Zn50Co+I₂+T, ZIF-67+I₂+T. Two additional experiments were carried out to trace the amorphization process during iodine sorption. First, we have focused on the iodine amount. In this way, we have used the ZIF-8 sample with iodine crystals with ratios ZIF-8 per I by weight – 1:0.5, 1:1, 1:2. Obtained samples were designated as ZIF-8+I₂-1, ZIF-8+I₂-2, ZIF-8+I₂-3, respectively (SI Table S3). Secondly, we have focused on the temperature of the iodine sorption. In this way, we have repeated iodine sorption experiments with ZIF-8 and ZIF-67 at 60 °C. So, we have obtained samples ZIF-8+I₂_60 and ZIF-67+I₂_60 (SI Table S3).

Before the iodine sorption experiment, all obtained samples were comprehensively characterized (Figure 1, Section 5 in SI) [30]. Observed properties were in good agreement with those reported previously [31-33]. All obtained samples had ZIF-8 structure type, according to XRPD (Figure 1a), and a specific surface area of more than 1450 m²/g (SI Table S4). Particle size in all cases was about 30-50 nm, according to TEM images (Figure 1c). A uniform distribution of Zn/Co ions was confirmed by EDX mapping (Figure 1b).

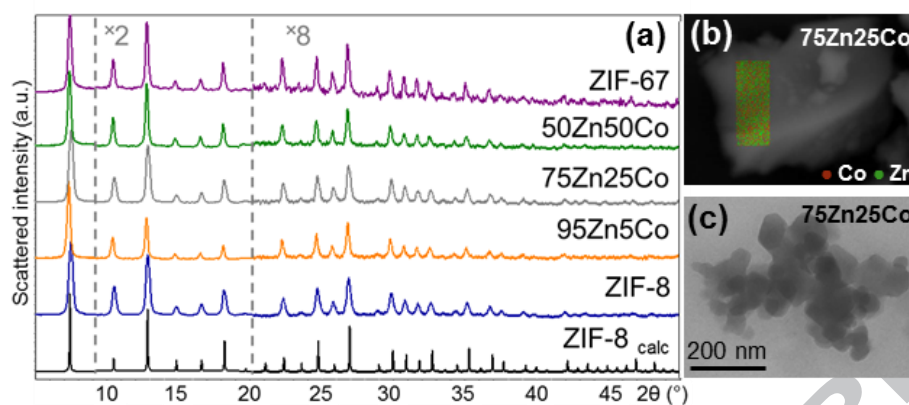


Figure 1 (a) XRPD profiles of synthesized ZIF-samples. (b) SEM image of 75Zn25Co sample with Zn/Co distribution: green dots represent Zn, red ones Co. (c) TEM image of 75Zn25Co sample.

After iodine sorption experiments, samples were characterized using XRPD, FTIR, TGA, XRF, and other techniques. All samples after iodine saturation become amorphous according to XRPD (SI Fig.S6 a-d, Figure 2a). After additional heating, the initial crystal structure was not observed anymore. As it was reported previously, ZIFs could form glasses, losing the long-range order, and at the same time preserving the initial short-range order and porosity [34, 35]. Moreover, amorphization of ZIF-8 samples during iodine sorption was observed at elevated temperatures [36], and it was claimed that amorphization prevents iodine release [37, 38]. To trace the amorphization process, we have varied temperature and iodine concentration (SI Table S3). According to these experiments, we could conclude that iodine concentration affects the amorphization process more than temperature does (SI Fig.S6e,f). We have observed a dramatic decrease of the specific surface area in the 75Zn25Co sample from 1523 m²/g to 14 m²/g after iodine saturation (Figure 2c). This could be attributed to filling pores with iodine molecules, in good agreement with EDX and XRF data revealing the presence of iodine (Figure 2b,d, Table 2, SI Fig.S7).

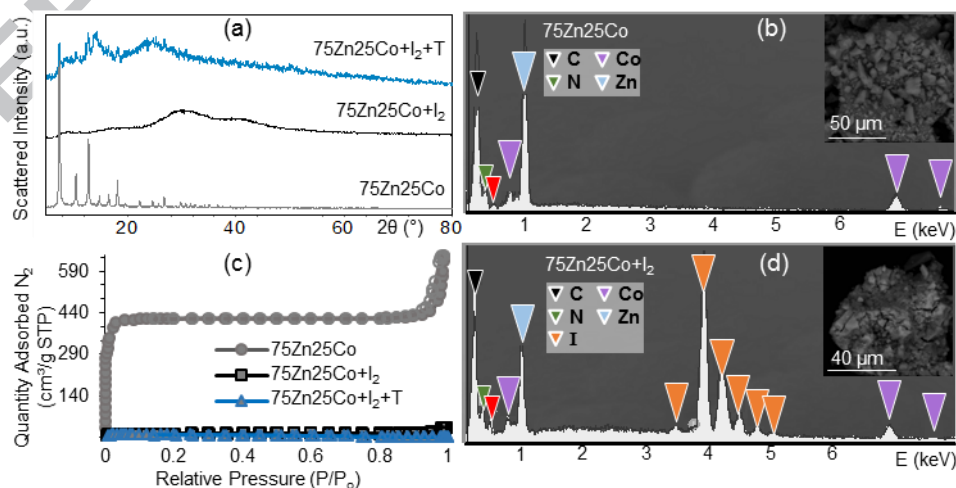


Figure 2 (a) XRPD profiles of the samples 75Zn25Co (gray), 75Zn25Co+I₂ (black), and 75Zn25Co+I₂+T (blue). Profiles are shifted along y-axes for better representation. EDX spectra of 75Zn25Co (b) and 75Zn25Co+I₂ samples (d); black triangles represent C peaks, green – N, red – O, purple – Co, blue – Zn, orange – I. Insets represent SEM images of investigated samples. (c) N₂ adsorption-desorption isotherms of the samples 75Zn25Co (circle markers), 75Zn25Co+I₂ (square markers), and 75Zn25Co+I₂+T (triangular markers). Filled markers correspond to adsorption branches of isotherms, empty– to desorption ones.

According to a careful analysis of FTIR spectra (Figure 3a, SI section 7), we could conclude that the most dramatic changes in the spectra after iodine saturation and after additional heating are attributed to the modes of the $-\text{CH}_3$ group of MIm. The intensity of the modes assigned to the individual vibrations of the methyl group decreased, while modes associated with the imidazole ring vibrations transformed from the “MIm-like” spectrum to the “Imidazole-like” spectrum. Moreover, an increase of cobalt content in the sample results in more pronounced changes in the spectra (Figure 3b,c, SI Fig. S7c). To highlight this trend, we have plotted difference spectra using the initial spectra as starting point and spectra after iodine saturation (Figure 3b) and after additional heating (Figure 3c), and we calculated the dependence of the integral intensities of the differential spectra from Zn content (SI Fig. S7c). This trend could be attributed to two steps of the iodine sorption process. The first step includes a “gate-opening” effect when MIm linkers spine around σ -bonds, and it enlarges windows into the pores. The spinning of the linker leads to an enhanced ring–ring interaction of the ZIF-8 framework within the unit cell. Higher stiffness of the Co-linker bonds in comparison with Zn-linker ones [39] results in a less flexible structure [40, 41]. So, in the ZIF-8 structure after iodine saturation, all MIm linkers are tilted, and methyl groups are not in the cavities, while in the less flexible ZIF-67 framework rotation of the linkers is obstructed and an interaction of the $-\text{CH}_3$ groups with the large polarized iodine molecules leads to changes in the FTIR spectra.

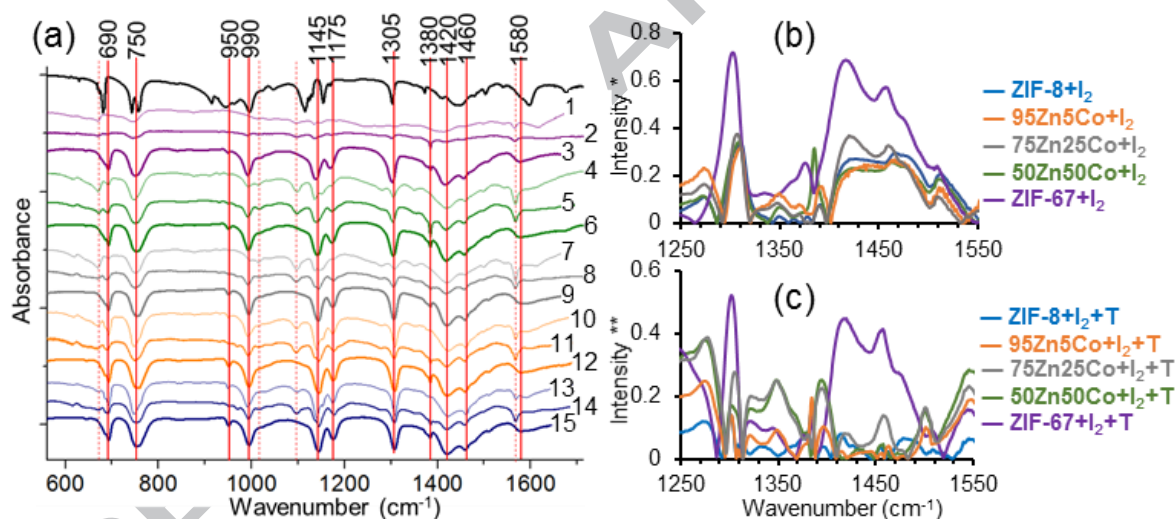


Figure 3 (a) FTIR spectra of all obtained samples: 1 – ZIF-67+I₂+T, 2 – ZIF-67+I₂, 3 – ZIF-67, 4 – 50Zn50Co+I₂+T, 5 – 50Zn50Co+I₂, 6 – 50Zn50Co, 7 – 75Zn25Co+I₂+T, 8 – 75Zn25Co+I₂, 9 – 75Zn25Co, 10 – 95Zn5Co+I₂+T, 11 – 95Zn5Co+I₂, 12 – 95Zn5Co, 13 – ZIF-8+I₂+T, 14 – ZIF-8+I₂, 15 – ZIF-8. The black curve represents the MIm spectrum. Differential plot calculated from the difference between spectra of initial ZIFs and the same samples after iodine saturation (b) and additional heating (c).

According to the TGA data, most of the adsorbed iodine molecules are located inside pores and could be evacuated only after decomposition of the framework (Figure 4). Iodine uptake increases with an increasing Zn^{2+} content in the structure (Table 2). In the same way, with an increasing zinc content, the temperature of iodine release increases as well.

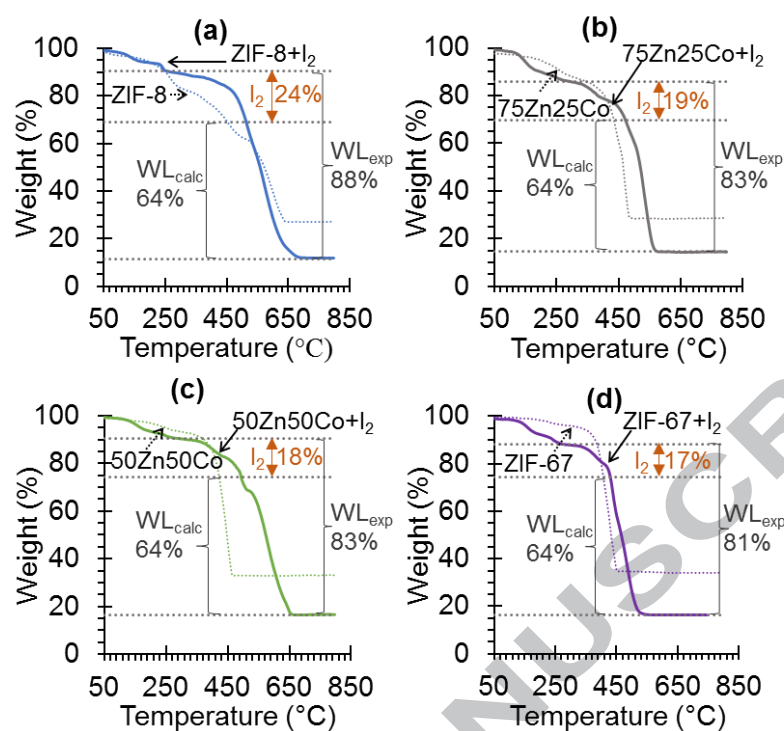


Figure 4 TGA curves of ZIF-8 and ZIF-8+I₂ (a), 75Zn25Co and 75Zn25Co+I₂ (b), 50Zn50Co and 50Zn50Co+I₂ (c), ZIF-67 and ZIF-67+I₂ (d) samples. Solid lines represent data for samples after iodine saturation, while dotted curves – for initial ZIF samples. WL_{exp} = Experimental weight loss for samples after iodine saturation; WL_{calc} = Calculated weight loss according to pure ZIF material (see details in section 8 of SI).

Table 2 Iodine uptake according to TGA and XRF measurements

Sample designation	TGA data				XRF iodine atomic %		Ratio Zn:Co XRF, atomic %	
	Weight % of I ₂	I ₂ molecules per cage	Mol % I/ZIF	Temperature of I ₂ release (°C)	Before heating	After heating	Zn ²⁺	Co ²⁺
ZIF-8+I ₂	23.6	0.84	42.3	485	39	40	100	0
95Zn5Co+I ₂	22.1	0.79	39.6	475	43	38	96	4
75Zn25Co+I ₂	19.2	0.68	34.1	475	44	36	79	21
50Zn50Co+I ₂	17.8	0.63	31.4	470	46	33	53	47
ZIF-67+I ₂	17.5	0.61	30.6	435	63	32	0	100

The external surface of the crystals could absorb a small part of the iodine molecules. We have observed that cobalt doping increases the amount of external iodine. To demonstrate it, we have measured the iodine content using XRF analysis just after the iodine sorption experiment and after heating at 250 °C for 2 h (Table 2). At this temperature, only iodine from the external surface could be removed. The difference in these two values for each sample increased with an increasing Co content. Therefore, substitution of zinc ions with cobalt ones resulted in a decrease of iodine uptake by the internal pores and at the same time in an increase of the part of iodine adsorbed by the external surface. This could be caused by the higher stiffness of the Co-linker bonds in comparison with Zn-linker ones [39] and as a result a less flexible structure [40, 41]. It could obstruct the transfer of the iodine molecules into the internal volume, leaving them on the external surface of the crystals. This hypothesis is in good agreement with results reported

previously [45]. Kwon et al. observed enhanced separating properties of ZIF-67 in comparison with ZIF-8. More rigid Co-N bonds decreased the effective pore aperture due to a smaller degree of the ligand flipping motion. The second trend observed in this work is a decrease in temperature of iodine release with an increasing cobalt content. This phenomenon is in good agreement with a small reduction of thermal stability of pure ZIF-67 in comparison with ZIF-8. We also have observed a slight decrease of Co content in comparison with the quantity used for synthesis (Table 2). Both aspects could be attributed to stronger coordination bonds between Zn and linker than between Co and linker [46].

We have investigated the effect of Zn^{2+} substitution by Co^{2+} in ZIF-8 on iodine capping properties. It was shown that all bi- and mono-metallic ZIFs with ZIF-8 structure adsorb iodine gas preferentially by internal pores and retain I_2 molecules up to framework collapse at temperatures higher than 400 °C. We have demonstrated that Co doping of ZIF-8 structure results in a decreasing iodine uptake by an internal pore volume and an increasing iodine uptake by an external surface of the crystals. We have attributed this phenomenon to the higher stiffness of the Co-MIm bonds in comparison with Zn-MIm bonds, which results in a less flexible structure. A hindered “gate-opening” effect leads to obstructed iodine transport from the external to the internal surface. FTIR measurements also confirmed the proposed explanation – modes attributed to $-CH_3$ groups were affected by iodine saturation much stronger in samples with high Co concentration. It indicates a stronger interaction of the adsorbed iodine molecules with methyl-groups of non-tilted MIm linkers. We also observed that higher cobalt content results in a decrease of iodine release temperature in good agreement with stronger coordination bonds Zn-linker compared to Co-linker. In this way, Co doping of the ZIF-8 structure allowed to tune the iodine adsorption properties with respect to the part of the iodine adsorbed by internal and external surfaces of the crystals and the temperature of iodine release.

VVB and EAB acknowledge RFBR for financial support according to the project №18-33-00584. The authors express their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through research groups program under grant number R.G.P.1/12/39.

References

- [1] Y. Muramatsu, S. Yoshida, U. Fehn, S. Amachi, Y. Ohmomo, Studies with natural and anthropogenic iodine isotopes: iodine distribution and cycling in the global environment, *J. Environ. Radioact.*, 74 (2004) 221-232.
- [2] J.A. Garland, R. Wakeford, Atmospheric emissions from the Windscale accident of October 1957, *Atmos. Environ.*, 41 (2007) 3904-3920.
- [3] X.L. Hou, V. Hansen, A. Aldahan, G. Possnert, O.C. Lind, G. Lujanienė, A review on speciation of iodine-129 in the environmental and biological samples, *Anal. Chim. Acta*, 632 (2009) 181-196.
- [4] Z. Jaworowski, OBSERVATIONS ON THE CHERNOBYL DISASTER AND LNT, Dose-Response, 8 (2010) 148-171.
- [5] V.S. Kazakov, E.P. Demidchik, L.N. Astakhova, THYROID-CANCER AFTER CHERNOBYL, *Nature*, 359 (1992) 21-21.
- [6] T. Sakurai, A. Takahashi, Y.E. Ming-lu, T. Kihara, S. Fujine, Trapping and Measuring Radioiodine (Iodine-129) in Cartridge Filters, *Journal of Nuclear Science and Technology*, 34 (1997) 211-216.
- [7] K. Munakata, S. Kanjo, S. Yamatsuki, A. Koga, D. Ianovski, Adsorption of Noble Gases on Silver-mordenite, *Journal of Nuclear Science and Technology*, 40 (2003) 695-697.
- [8] K.W. Chapman, P.J. Chupas, T.M. Nenoff, Radioactive Iodine Capture in Silver-Containing Mordenites through Nanoscale Silver Iodide Formation, *J. Am. Chem. Soc.*, 132 (2010) 8897-+.

- [9] S.M. Scott, T. Hu, T.K. Yao, G.Q. Xin, J. Lian, Graphene-based sorbents for iodine-129 capture and sequestration, *Carbon*, 90 (2015) 1-8.
- [10] K.S. Subrahmanyam, D. Sarma, C.D. Malliakas, K. Polychronopoulou, B.J. Riley, D.A. Pierce, J. Chun, M.G. Kanatzidis, Chalcogenide Aerogels as Sorbents for Radioactive Iodine, *Chem. Mat.*, 27 (2015) 2619-2626.
- [11] J.H. Yang, J.M. Shin, J.J. Park, G. Il Park, M.S. Yim, Novel synthesis of bismuth-based adsorbents for the removal of I-129 in off-gas, *J. Nucl. Mater.*, 457 (2015) 1-8.
- [12] S.U. Nandanwar, K. Coldsnow, V. Utgikar, P. Sabharwall, D.E. Aston, Capture of harmful radioactive contaminants from off-gas stream using porous solid sorbents for clean environment - A review, *Chem. Eng. J.*, 306 (2016) 369-381.
- [13] J. Li, J.T. Li, A luminescent porous metal-organic framework with Lewis basic pyridyl sites as a fluorescent chemosensor for TNP detection, *Inorg. Chem. Commun.*, 89 (2018) 51-54.
- [14] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, The Chemistry and Applications of Metal-Organic Frameworks, *Science*, 341 (2013) 974-+.
- [15] H. Qu, L. Qiu, X.K. Leng, M.M. Wang, S.M. Lan, L.L. Wen, D.F. Li, Structures and photocatalytic activities of metal-organic frameworks derived from rigid aromatic dicarboxylate adds and flexible imidazole-based linkers, *Inorg. Chem. Commun.*, 14 (2011) 1347-1351.
- [16] M. Guo, H.L. Cai, R.G. Xiong, Ferroelectric metal organic framework (MOF), *Inorg. Chem. Commun.*, 13 (2010) 1590-1598.
- [17] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Reticular synthesis and the design of new materials, *Nature*, 423 (2003) 705-714.
- [18] V.V. Butova, M.A. Soldatov, A.A. Guda, K.A. Lomachenko, C. Lamberti, Metal-organic frameworks: structure, properties, methods of synthesis and characterization, *Russ. Chem. Rev.*, 85 (2016) 280-307.
- [19] M.H. Zeng, Q.X. Wang, Y.X. Tan, S. Hu, H.X. Zhao, L.S. Long, M. Kurmoo, Rigid Pillars and Double Walls in a Porous Metal-Organic Framework: Single-Crystal to Single-Crystal, Controlled Uptake and Release of Iodine and Electrical Conductivity, *J. Am. Chem. Soc.*, 132 (2010) 2561.
- [20] W.W. He, S.L. Li, G.S. Yang, Y.Q. Lan, Z.M. Su, Q. Fu, Controllable synthesis of a non-interpenetrating microporous metal-organic framework based on octahedral cage-like building units for highly efficient reversible adsorption of iodine, *Chem. Commun.*, 48 (2012) 10001-10003.
- [21] A.K. Chaudhari, S. Mukherjee, S.S. Nagarkar, B. Joarder, S.K. Ghosh, Bi-porous metal-organic framework with hydrophilic and hydrophobic channels: selective gas sorption and reversible iodine uptake studies, *Crystengcomm*, 15 (2013) 9465-9471.
- [22] D.F. Sava, K.W. Chapman, M.A. Rodriguez, J.A. Greathouse, P.S. Crozier, H.Y. Zhao, P.J. Chupas, T.M. Nenoff, Competitive I-2 Sorption by Cu-BTC from Humid Gas Streams, *Chem. Mat.*, 25 (2013) 2591-2596.
- [23] J. He, J.J. Duan, H.T. Shi, J. Huang, J.H. Huang, L. Yu, M. Zeller, A.D. Hunter, Z.T. Xu, Immobilization of Volatile and Corrosive Iodine Monochloride (ICI) and I-2 Reagents in a Stable Metal-Organic Framework, *Inorg. Chem.*, 53 (2014) 6837-6843.
- [24] J. Wang, J.H. Luo, X.L. Luo, J. Zhao, D.S. Li, G.H. Li, Q.S. Huo, Y.L. Liu, Assembly of a Three-Dimensional Metal Organic Framework with Copper(I) Iodide and 4-(Pyrimidin-5-yl) Benzoic Acid: Controlled Uptake and Release of Iodine, *Cryst. Growth Des.*, 15 (2015) 915-920.
- [25] G. Mehlana, G. Ramon, S.A. Bourne, A 4-fold interpenetrated diamondoid metal-organic framework with large channels exhibiting solvent sorption properties and high iodine capture, *Microporous Mesoporous Mat.*, 231 (2016) 21-30.
- [26] Y.Q. Hu, M.Q. Li, Y.Y. Wang, T. Zhang, P.Q. Liao, Z.P. Zheng, X.M. Chen, Y.Z. Zheng, Direct Observation of Confined I-center dot center dot center dot I-2 center dot center dot center dot I- Interactions in a Metal-Organic Framework: Iodine Capture and Sensing, *Chem.-Eur. J.*, 23 (2017) 8409-8413.

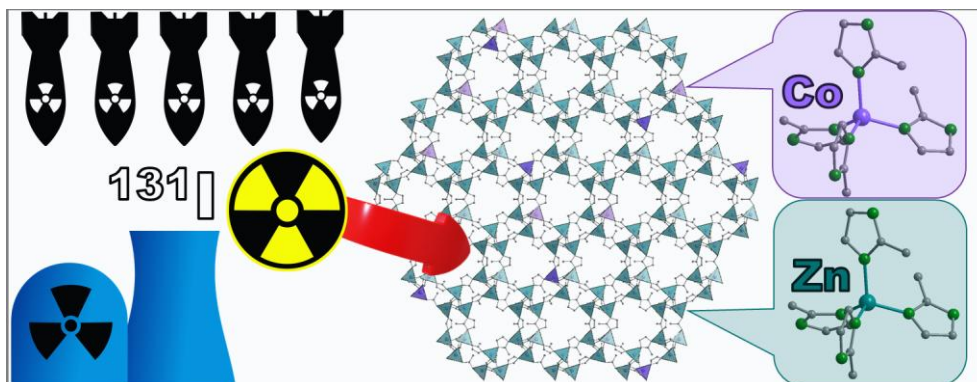
- [27] D.F. Sava, M.A. Rodriguez, K.W. Chapman, P.J. Chupas, J.A. Greathouse, P.S. Crozier, T.M. Nenoff, Capture of Volatile Iodine, a Gaseous Fission Product, by Zeolitic Imidazolate Framework-8, *J. Am. Chem. Soc.*, 133 (2011) 12398-12401.
- [28] J.T. Hughes, D.F. Sava, T.M. Nenoff, A. Navrotsky, Thermochemical Evidence for Strong Iodine Chemisorption by ZIF-8, *J. Am. Chem. Soc.*, 135 (2013) 16256-16259.
- [29] V.V. Butova, A.P. Budnyk, E.A. Bulanova, A.V. Soldatov, New microwave-assisted synthesis of ZIF-8, *Mendeleev Commun.*, 26 (2016) 43-44.
- [30] V.V. Butova, V.A. Polyakov, A.P. Budnyk, A.M. Aboaraia, E.A. Bulanova, A.A. Guda, E.A. Reshetnikova, Y.S. Podkovyrina, C. Lamberti, A.V. Soldatov, Zn/Co ZIF family: MW synthesis, characterization and stability upon halogen sorption, *Polyhedron*, 154 (2018) 457-464.
- [31] Y. Hu, H. Kazemian, S. Rohani, Y.N. Huang, Y. Song, In situ high pressure study of ZIF-8 by FTIR spectroscopy, *Chem. Commun.*, 47 (2011) 12694-12696.
- [32] D. Saliba, M. Ammar, M. Rammal, M. Al-Ghoul, M. Hmadeh, Crystal Growth of ZIF-8, ZIF-67, and Their Mixed-Metal Derivatives, *J. Am. Chem. Soc.*, 140 (2018) 1812-1823.
- [33] V.V. Butova, A.P. Budnyk, E.A. Bulanova, C. Lamberti, A.V. Soldatov, Hydrothermal synthesis of high surface area ZIF-8 with minimal use of TEA, *Solid State Sci.*, 69 (2017) 13-21.
- [34] R. Gaillac, P. Pullumbi, F.X. Coudert, Melting of Zeolitic Imidazolate Frameworks with Different Topologies: Insight from First-Principles Molecular Dynamics, *J. Phys. Chem. C*, 122 (2018) 6730-6736.
- [35] L. Frenzel-Beyme, M. Kloss, R. Pallach, S. Salamon, H. Moldenhauer, J. Landers, H. Wende, J. Debus, S. Henke, Porous purple glass - a cobalt imidazolate glass with accessible porosity from a meltable cobalt imidazolate framework, *J. Mater. Chem. A*, 7 (2019) 985-990.
- [36] L.J. Small, T.M. Nenoff, Direct Electrical Detection of Iodine Gas by a Novel Metal-Organic-Framework-Based Sensor, *ACS Appl. Mater. Interfaces*, 9 (2017) 44649-44655.
- [37] K.W. Chapman, D.F. Sava, G.J. Halder, P.J. Chupas, T.M. Nenoff, Trapping Guests within a Nanoporous Metal-Organic Framework through Pressure-Induced Amorphization, *J. Am. Chem. Soc.*, 133 (2011) 18583-18585.
- [38] T.D. Bennett, P.J. Saines, D.A. Keen, J.C. Tan, A.K. Cheetham, Ball-Milling-Induced Amorphization of Zeolitic Imidazolate Frameworks (ZIFs) for the Irreversible Trapping of Iodine, *Chem.-Eur. J.*, 19 (2013) 7049-7055.
- [39] Y. Yuan, X.Q. Dong, Y.F. Chen, M.H. Zhang, Computational screening of iodine uptake in zeolitic imidazolate frameworks in a water-containing system, *Phys. Chem. Chem. Phys.*, 18 (2016) 23246-23256.
- [40] Z.W. Hu, Z.Y. Guo, Z.P. Zhang, M.L. Dou, F. Wang, Bimetal Zeolitic Imidazolite Framework-Derived Iron-, Cobalt- and Nitrogen-Codoped Carbon Nanopolyhedra Electrocatalyst for Efficient Oxygen Reduction, *ACS Appl. Mater. Interfaces*, 10 (2018) 12651-12658.
- [41] P. Krokidas, S. Moncho, E.N. Brothers, M. Castier, I.G. Economou, Tailoring the gas separation efficiency of metal organic framework ZIF-8 through metal substitution: a computational study, *Phys. Chem. Chem. Phys.*, 20 (2018) 4879-4892.
- [42] D. Fairen-Jimenez, S.A. Moggach, M.T. Wharmby, P.A. Wright, S. Parsons, T. Düren, Opening the Gate: Framework Flexibility in ZIF-8 Explored by Experiments and Simulations, *J. Am. Chem. Soc.*, 133 (2011) 8900-8902.
- [43] M.E. Casco, Y.Q. Cheng, L.L. Daemen, D. Fairen-Jimenez, E.V. Ramos-Fernandez, A.J. Ramirez-Cuesta, J. Silvestre-Albero, Gate-opening effect in ZIF-8: the first experimental proof using inelastic neutron scattering, *Chem. Commun.*, 52 (2016) 3639-3642.
- [44] S. Ohsaki, S. Watanabe, H. Tanaka, M.T. Miyahara, Free Energy Analysis for Adsorption-Induced Structural Transition of Colloidal Zeolitic Imidazolate Framework-8 Particles, *J. Phys. Chem. C*, 121 (2017) 20366-20374.
- [45] H.T. Kwon, H.-K. Jeong, A.S. Lee, H.S. An, J.S. Lee, Heteroepitaxially Grown Zeolitic Imidazolate Framework Membranes with Unprecedented Propylene/Propane Separation Performances, *J. Am. Chem. Soc.*, 137 (2015) 12304-12311.

[46] C.Q. Wang, F.Q. Yang, L.Q. Sheng, J. Yu, K.X. Yao, L.X. Zhang, Y.C. Pan, Zinc-substituted ZIF-67 nanocrystals and polycrystalline membranes for propylene/propane separation, *Chem. Commun.*, 52 (2016) 12578-12581.

ACCEPTED MANUSCRIPT

- The effect of Co^{2+} doping of ZIF-8 on iodine adsorption was investigated
- Co^{2+} doping decreases iodine uptake by an internal pore volume
- Co^{2+} doping increases iodine uptake by an external surface of the crystals
- Higher Co^{2+} content decreases temperature of iodine release

ACCEPTED MANUSCRIPT



ACCEPTED MANUSCRIPT