

## FTIR study of modification of transition metal on zeolites for adsorption

Belgin Bardakçi<sup>1\*</sup> & Semiha Bahçeli<sup>2</sup>

<sup>1</sup>Faculty of Arts and Sciences, Physics Department, Mehmet Akif Ersoy University, Burdur, 15030, Turkey

<sup>2</sup>Faculty of Arts and Sciences, Physics Department, Süleyman Demirel University, Isparta, 32260, Turkey

\*E-mail: bbardakci@mehmetakif.edu.tr

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Adsorption of 1-propanethiol on  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  modified, synthetic (3A, 4A and 13X) zeolites were studied by FTIR (Fourier Transform Infrared) spectroscopy and SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-Ray) graphics. Amount of metal cations on mentioned zeolites was measured by AAS (Atomic Absorption Spectrometer). Based on divalent cations of zeolites, it was assumed that cations may affect their adsorption properties. The nature of the cations present in a given type zeolite markedly affects the physical and chemical feature of the system, for instance, valance and size of cations and their location in the zeolite framework influence adsorption, molecular sieving and catalytic properties. In this study, we used cation exchanged zeolites as adsorbents due to their high surface area. Zeolites with divalent cations show an affinity to adsorb 1-propanethiol comparing to their ordinary positions with monovalent cations. The lack of S-H band in IR spectra gives an idea, that sulphur may make a bond to metal ( $\text{Cd}^{2+}$  or  $\text{Co}^{2+}$ ) or it makes a bond to H atom of isolated OH groups of zeolite surface.

**Keywords:** Zeolite, 1-propanethiol, Cation-exchange, Adsorption, FTIR spectroscopy

### 1 Introduction

Zeolites are made up of three-dimensional framework of alumina ( $\text{AlO}_4$ ) and silica ( $\text{SiO}_4$ ) molecules. The excess oxygen in the alumina molecules gives the framework of a negative charge which can be balanced by trapping positively-charged ions (cations) in cages of the structure. They have the ability to hold heavy metals; and especially transition metal loaded zeolites, with their large surface area, acidic and shape selective properties support adsorption<sup>1</sup>. Studies on the ion exchange properties of zeolites are critical to their uses as sorbents and catalysts, and much investigation has been carried out<sup>2-5</sup>. Since zeolite selectivity theory predicts divalent cations are more likely to be selected over monovalent cations<sup>6</sup>. This theory forced us to choose KA, NaA and NaX zeolites (all of them have monovalent cations). Hence, these are promising candidate to be exchanged with the cations  $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$  cations (divalent cations). To monitor the influence of some heavy metals cations on the zeolites, we used SEM-EDX graphics as well as FTIR; this method had been used before by other scientists<sup>7</sup>. The applications of vibrational spectroscopic techniques for investigating different environmental problems have grown significantly in the last years<sup>8-10</sup>. 1-propanethiol is one of the main mercaptan compounds in fuel oil. Removal of

1-propanethiol is an important factor for pollution in case of spills of oils in marine<sup>11</sup>. It is also used for protection of metal corrosion on a surface and usually increases hydrophobicity of the surface<sup>12</sup>. Zeolites with their 30-50% void space after dehydration and contain uniform sized pores, provide a capability to control interaction with any molecules from outside. They are also known as molecular sieves. Their structures provide unique studies. Developing the physical and chemical properties of zeolites (molecular sieves) in order to meet the needs is one of the most advanced and favorite applications of zeolites in industry. In this study, the adsorption of 1-propanethiol (1-PT) on cadmium and cobalt modified synthetic 3A, 4A and 13X zeolites has been investigated.

### 2 Experimental Details

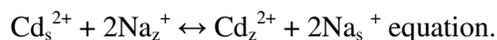
Synthetic 3A, 4A and 13X zeolites were purchased from Aldrich Chemical Company. The unit cell of the zeolite 4A consists of  $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}].27\text{H}_2\text{O}$ . Zeolite 3A is potassium exchanged form of 4A zeolite. Unit cell of 13X zeolite is  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}].264\text{H}_2\text{O}$ . They were activated at 623 K for 4 h and then they were modified by impregnation method with corresponding cadmium chloride and cobalt nitrate salts. 0.2 M of cobalt nitrate and cadmium chloride solutions were prepared

by using distilled water (The Millipore purified (18.2 mΩ cm) water was used in all experiments) after that, 40 cm<sup>3</sup> of each solution was added to 0.5 g of activated zeolites, respectively. Samples were stored and stirred for 24 h and then filtered and dried at room temperature. The metal contents of the modified zeolites were analyzed by using a Perkin-Elmer AAS 800 Analyst instrument. For adsorption process, we used the same method which was used in our previous work<sup>13</sup>. After transition metal cations were supported on the zeolite, SEM images of samples were acquired on a JEOL SEM 5600 equipped with EDX (an energy dispersive X-ray analyzer). FTIR measurements were performed on a Perkin-Elmer BX II FTIR spectrometer using the KBr self-supported pellet technique. The pellets contained about 1% of powdered sample and were pressed at 3 or 4 ton/cm<sup>2</sup>.

### 3 Results and Discussion

The adsorption process of 1-PT on activated synthetic 3A, 4A and 13X zeolites has been studied. But monitoring of adsorption of samples by IR spectroscopy indicated that the adsorption process failed. After that, considering the failure, hopefully, modified synthetic zeolites with divalent cations may influence the adsorption. 1-PT effect on formation of SAM (self-assembled monolayer) along Au (Ref. 14), GaAs (Ref. 15) surface had been studied before. The adsorption of 1-PT on copper surface<sup>16</sup> and silver film<sup>17,18</sup> was investigated by other researchers. Then,

zeolites were modified with Co<sup>2+</sup> and Cd<sup>2+</sup> cations. The amount of mentioned cations on 3A, 4A, 13X zeolites and stock solution are presented in Table 1. The results show that zeolites are modified by exchanging their monovalent cations with Co<sup>2+</sup> and Cd<sup>2+</sup> cations. When exchanging ions of unequal charge, as is the case the exchange of zeolitic Na<sup>+</sup> with solution phase Cd<sup>2+</sup> or Co<sup>2+</sup>, the exchange equilibrium for, as an example, the Cd/NaX system can be represented by :



(where the subscripts s and z refer to the “solution” and “zeolite” phases, respectively).

IR spectral results of 1-PT adsorbed on Co<sup>2+</sup> and Cd<sup>2+</sup> modified zeolites are shown in Figs 1 and 2, respectively. FT-IR spectra of Cd/zeolite or Co/zeolite samples prepared by ion exchange are similar to the spectra of naked zeolites. The IR spectra of cobalt, cadmium modified zeolites also present the characteristic bands of zeolites although a slight

Table 1 — Amount of metal cation in zeolites and stock solution (mg/l)

Samples	Cd (ppm)	Co (ppm)
Stock	14620	11470
3A	13950	11040
4A	13640	10950
13X	14180	11140

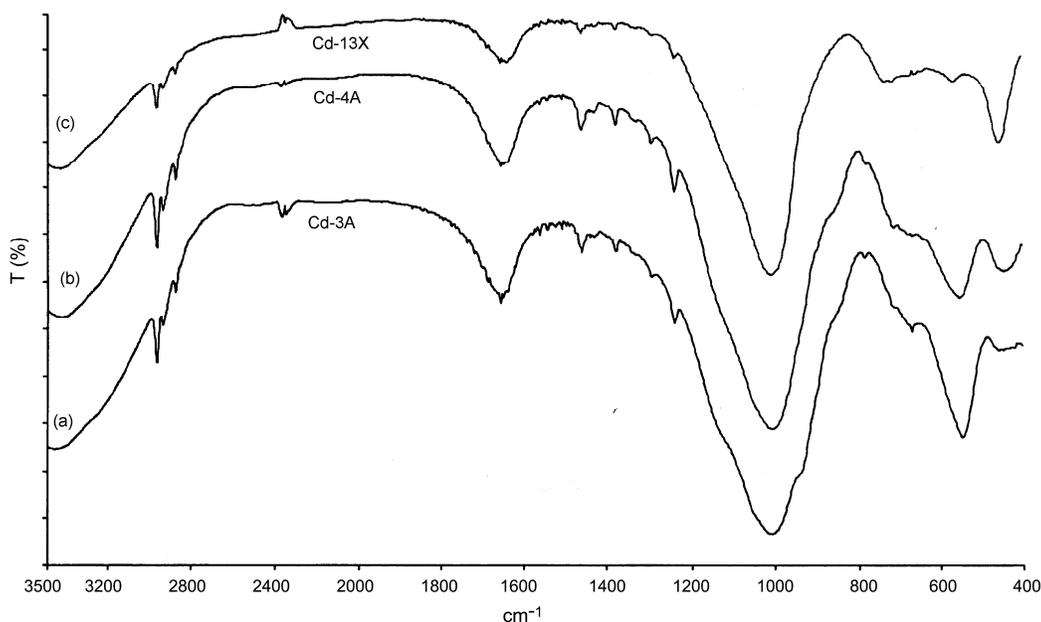


Fig. 1 — IR spectra of 1-PT adsorbed on cadmium modified a) type 3A b) type 4A c) type 13X zeolite

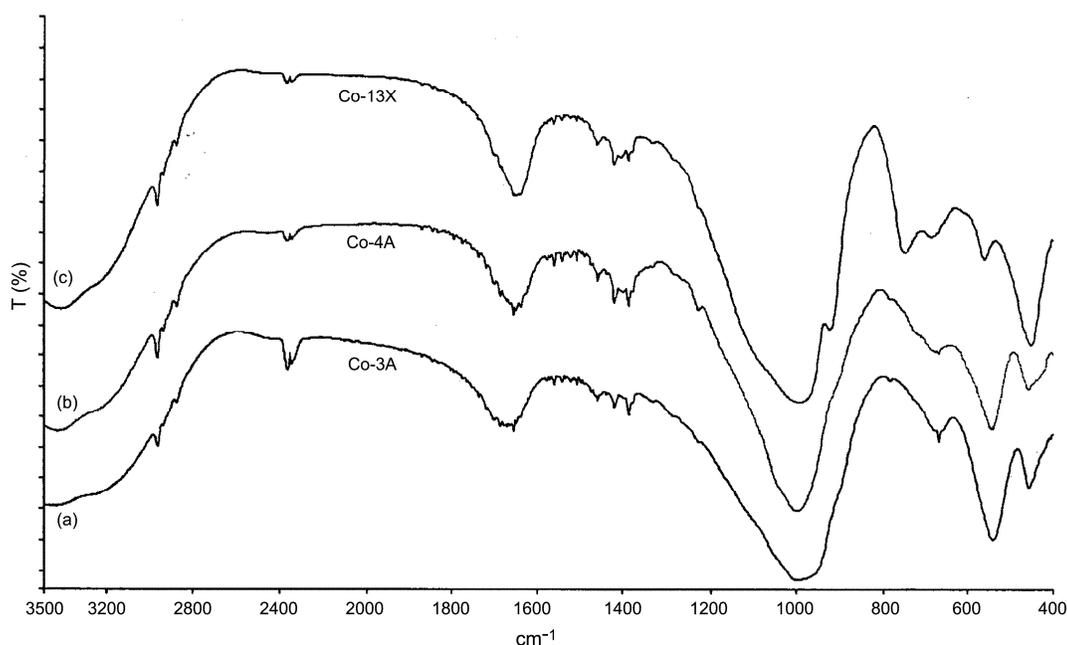


Fig. 2 — IR spectra of 1-PT adsorbed on cobalt modified a) type 3A b) type 4A c) type 13X zeolite

Table 2 — IR frequencies ( $\text{cm}^{-1}$ ) of 1-PT adsorbed on cadmium supported 3A, 4A and 13X zeolites

Pure 1-PT	Assignment	Adsorbed 1-PT on Cd modified zeolites		
		3A	4A	13X
2961 s	CH <sub>3</sub> and CH <sub>2</sub> str.	2960 m	2960 m	2960 m
2930 vs	CH <sub>3</sub> and CH <sub>2</sub> str.	2931 w	2930 w	2933 w
2872 s	CH <sub>3</sub> and CH <sub>2</sub> str.	2870 w	2870 m	2871 w
1456 s	CH <sub>3</sub> asymmetric defor.	1458 m	1458 m	1458 m
1438 s	CH <sub>2</sub> scissor.	1436 vw	1429 w	1430 vw
1376 s	CH <sub>3</sub> symmetric defor.	1375 w	1376 m	1376 w
1338 m	CH <sub>2</sub> wagging	1337 vw	1329 vw	1329 bw
1297 s	CH <sub>2</sub> wagging	1293 w	1291 w	1291 w
1246 s	CH <sub>2</sub> bending	1238 m	1238 m	1237 w
1106 s	CC str.	1133 bsh	1125 bsh	1126 bsh
1055 vw	CC str.	1054 bsh	1050 bsh	—
894 m	CH <sub>2</sub> rocking	—	895 bsh	—
878 m	CH <sub>2</sub> rocking	851 bsh	857 bsh	—
792 m	CSH def.	784 w	782 sh	782 bsh
731 s	CH <sub>2</sub> rocking	733 sh	—	733 vw
704 m	CS str.	717 sh	715 sh	717 vw

s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, bsh: broad shoulder, bw: broad weak

Table 3 — IR frequencies ( $\text{cm}^{-1}$ ) of 1-PT adsorbed on cobalt supported 3A, 4A and 13X zeolites

Pure 1-PT	Assignment	Adsorbed of 1-PT on Co modified zeolites		
		3A	4A	13X
2961 s	CH <sub>3</sub> and CH <sub>2</sub> str.	2959 m	2959 m	2960 m
2930 vs	CH <sub>3</sub> and CH <sub>2</sub> str.	2931 w	2931 w	2932 w
2872 s	CH <sub>3</sub> and CH <sub>2</sub> str.	2872 w	2871 w	2871 w
1456 s	CH <sub>3</sub> asymmetric defor.	1458 m	1457 m	1458 w
1438 s	CH <sub>2</sub> scissor.	1437 vw	1436 w	1437 vw
1376 s	CH <sub>3</sub> symmetric defor.	1374 sh	1375 sh	1375 sh
1338 m	CH <sub>2</sub> wagging	1339 sh	1340 vw	1329 w
1297 s	CH <sub>2</sub> wagging	1284 sh	1279 sh	1279 sh
1216 s	CH <sub>2</sub> bending	1227 sh	1226 w	1229 sh
1106 s	CC str.	1126 bsh	—	—
1055 vw	CC str.	1055 bsh	1045 bsh	—
894 m	CH <sub>2</sub> rocking	—	897 bsh	919 w
836 w	CH <sub>2</sub> rocking	—	829 sh	830 bsh
792 m	CSH def.	783 w	782 w	—
731 s	CH <sub>2</sub> rocking	728 sh	727 sh	747 m

s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, bsh: broad shoulder, bw: broad weak

change in the intensity of the bands has been noticed. These observations indicate that the framework of the zeolite is still firm. The IR spectral data of 1-PT adsorbed on Cd and Co modified synthetic zeolites are presented in Tables 2 and 3, respectively. The chemical formula of 1-propanethiol (1-PT) is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$  and has a chain structure. It can be

shown<sup>19</sup> either as 1-PT or n-PrSH. IR spectral assignments of 1-PT were made according to the reported data<sup>20-23</sup>. The bands between 2958 and 2867  $\text{cm}^{-1}$  can be attributed to methyl and methylene groups of 1-PT adsorbed on synthetic zeolites. The absence of S-H stretching vibration peak at 2558  $\text{cm}^{-1}$  which is the characteristic of 1-PT,

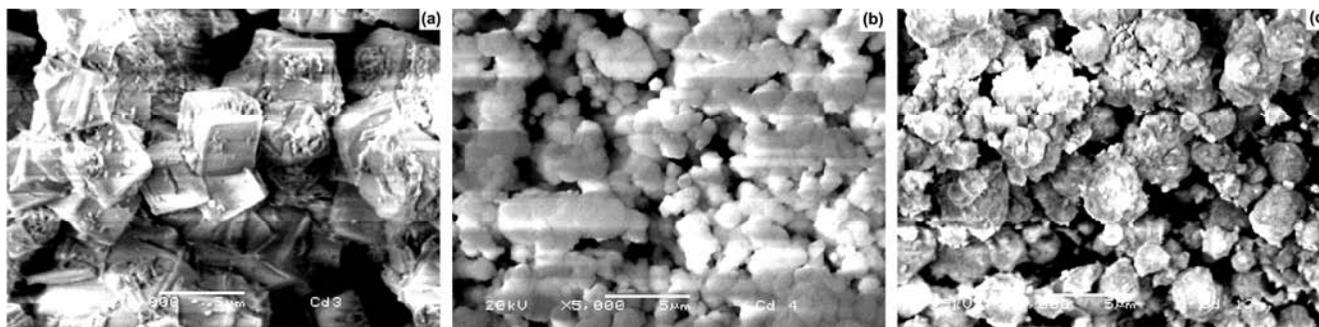


Fig. 3 — SEM image of cadmium supported (a) 3A zeolite, (b) 4A zeolite and (c) 13X zeolite

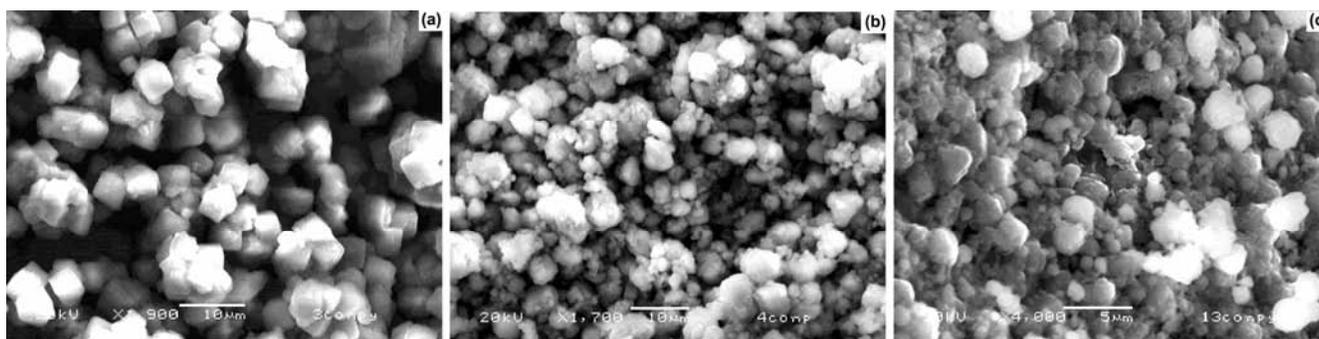


Fig. 4 — SEM image of cobalt modified (a) 3A zeolite, (b) 4A zeolite and (c) 13X zeolite

indicated that this band shifted to  $3350\text{--}3600\text{ cm}^{-1}$  by making a bond to H atom of isolated OH groups<sup>24</sup>. In Table 2, new band at  $1456\text{ cm}^{-1}$  due to  $\text{CH}_3$  asymmetric deformation band appeared after adsorption process. The methylene wagging band at  $1338\text{ cm}^{-1}$  of pure 1-PT was observed at  $1339$ ,  $1340$  and  $1329\text{ cm}^{-1}$  on 1-PT adsorbed 3A, 4A and 13X zeolites, respectively.

In Table 3,  $\text{CH}_2$  wagging vibration of 1-PT at  $1297\text{ cm}^{-1}$  shifted to lower frequency at  $1284\text{ cm}^{-1}$  for Co-3A zeolite after adsorption and the same band is observed at  $1279\text{ cm}^{-1}$  for cobalt modified 4A and 13X zeolite.

This result is agreed well with 1-propanethiol reaction on nickel surface<sup>25</sup>. In Table 2, the medium band at  $792\text{ cm}^{-1}$  is CSH deformation band. Related to this band, the appearance of weak band at  $784\text{ cm}^{-1}$  on Cd modified 3A zeolite, shoulders at  $782\text{ cm}^{-1}$  for 4A zeolite and 13X zeolite after adsorption process verified the adsorption on zeolite surface. Another sulphur bond at  $704\text{ cm}^{-1}$  occurred at  $717$ ,  $715$  and  $717\text{ cm}^{-1}$  for 3A, 4A and 13X zeolites in Table 2, respectively. But this band was not observed for 1-PT adsorbed Co modified zeolites. SEM images of cadmium supported zeolites have been shown in Fig. 3(a, b and c) for 3A, 4A and 13X zeolite, respectively. These of cobalt modified zeolites have

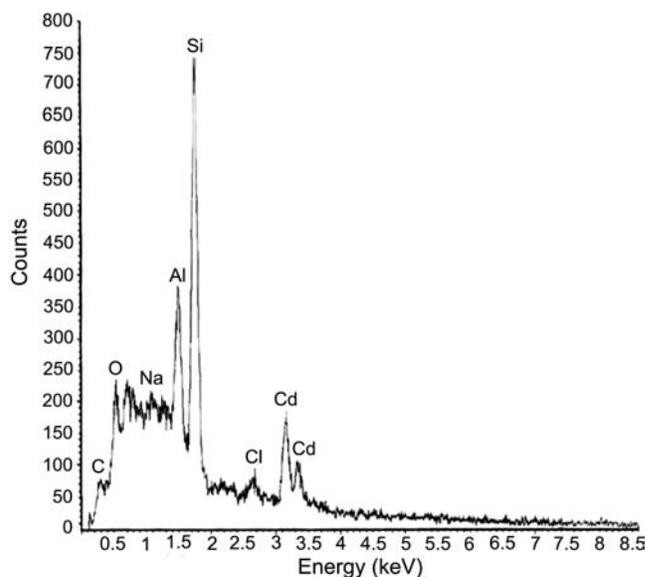


Fig. 5 — EDX graph of cadmium modified 4A zeolite before 1-PT adsorption

been shown in Fig. 4(a, b and c), for mentioned zeolites, respectively.

Cubic geometry of zeolite 3A has not changed much; neither cadmium nor cobalt modified zeolites. SEM (Scanning Electron Micrograph) of metal cation exchanged zeolite indicate well-defined crystals, in other words, modified metal does not affect the main structure of zeolite. The idea was supported with IR

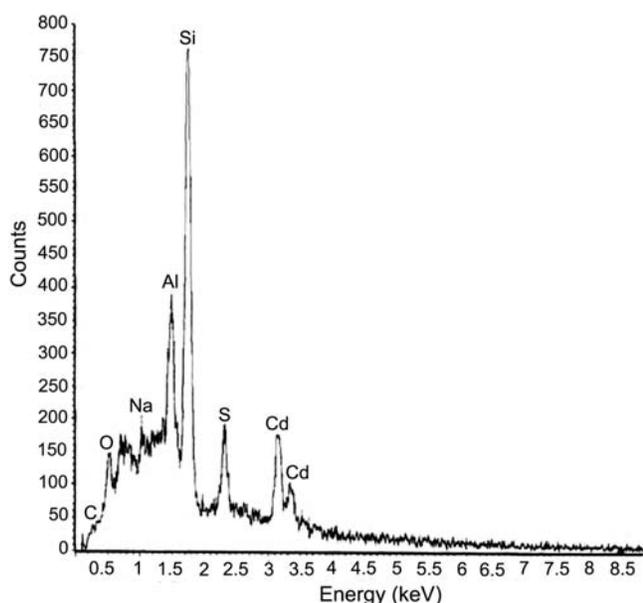


Fig. 6 — EDX graph of cadmium modified 4A zeolite after 1-PT adsorption

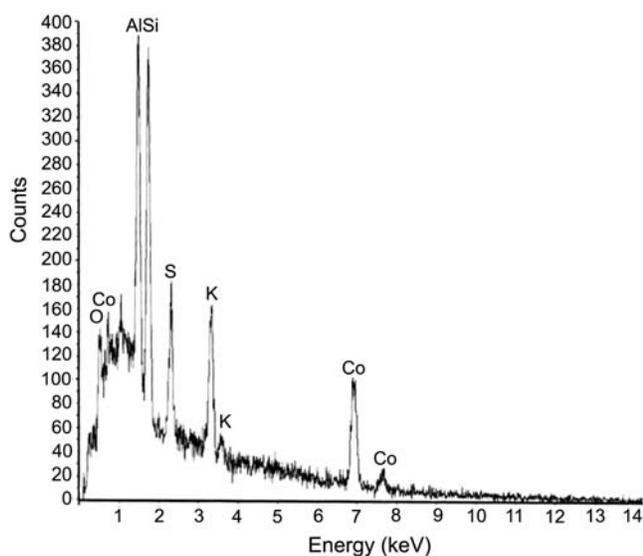


Fig. 7 — EDX graph of cobalt modified 3A zeolite after 1-PT adsorption

spectral results. The vibrational frequencies of metal cations modified zeolites show some slight differences with those of framework of pure zeolites. Bright part of SEM image shows metallic density of the zeolite surface. Morphology is still uniform throughout each metal-zeolite samples. Zeolite after ion-exchanged process, in the presence of cadmium or cobalt had the same morphology as pure zeolites. Figures 5 and 6 show the EDX graph of same sample before and after 1-PT adsorption on Cd-4A zeolite. In details, S peak observed in Fig. 6 confirmed the 1-PT

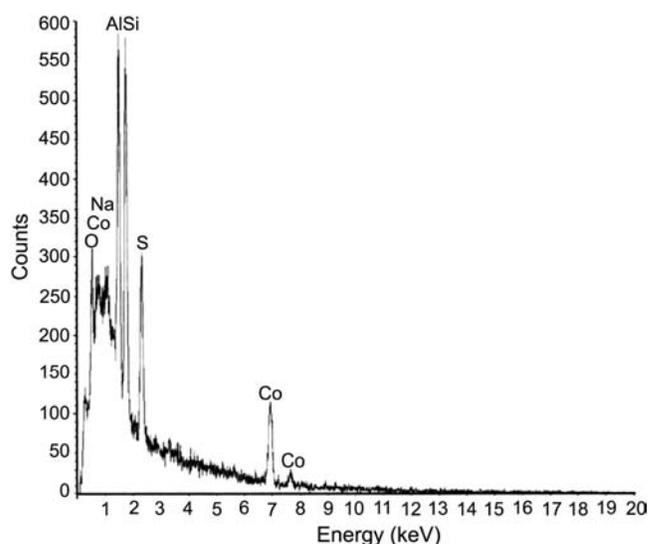


Fig. 8 — EDX graph of cobalt modified 4A zeolite after 1-PT adsorption

on metal modified surface. EDX graphs of 1-PT adsorbed on cobalt modified 3A and 4A zeolites are shown in Figs 7 and 8.

#### 4 Conclusions

Partial exchange of potassium (for 3A zeolite), sodium (for 4A zeolite and for 13X zeolite) ions in mentioned zeolites with divalent cations ( $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$ ) does not affect the structure of zeolite's framework. The exchange of cations can increase the diameter of cavity among zeolites. Hence, 1-propanethiol can interact with mentioned zeolites<sup>26</sup>. The transition metal cation supported zeolites indicate a synergism to adsorb 1-PT.  $\text{CH}_2$  wagging vibration of 1-PT shifted to lower frequencies as observed by Neff and others<sup>25</sup>. In this study, they did not use any matrix like zeolite, nickel surface was sufficient to observe some characteristic band of 1-PT. As a result, it can be predicted that not zeolite itself but metal surface on zeolite is a factor for adsorption of 1-PT. The functional groups studied by FTIR indicated that  $\text{CH}_2$  and  $\text{CH}_3$  groups were the main functional groups on zeolites after adsorption process. Divalent cations supported zeolites are favourable to attract metal ion. The alteration in composition of the cations may produce some remarkable changes in zeolite properties, such as pore size, catalytic activity<sup>27</sup>. Adsorption properties of zeolites are related to the type, number and location of their accessible cations<sup>28</sup>. In cation exchange system, metal cation can make a bond via oxygen of zeolite lattice. The appearance of the bands of 1-PT adsorbed on

modified zeolites is considered to be due to the coordination of 1-PT on cationic sites of modified zeolites. To clarify the effect of cadmium and cobalt ions exchanged in mentioned zeolites, for adsorption of 1-PT, explaining step by step, 1-PT adsorption was tried on activated zeolites but it was inconclusive. Then, after divalent cation exchanged, the adsorption process occurred. Cadmium or cobalt ion-exchanged sites in zeolites act as active sites for 1-PT adsorption. The absence of S–H stretching band at  $2558\text{ cm}^{-1}$  in spectra can be explained by the breaking of S–H bond and the S atoms may be directly bonded with cadmium or cobalt atoms on surface of zeolite. This result is consistent with the previous work<sup>29</sup> which can be explained by the following mechanism: oxidative cleavage of the S–H bonds of alkanethiol molecules is accompanied by formation of the metal-sulphur (M-S) bonds.

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