FT-IR Spectroscopic Study of 1,5-Pentanedithiol and 1,6-Hexanedithiol Adsorbed on NaA, CaA and NaY Zeolites

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The adsorption of 1,5-pentanedithiol (1,5-PDT) and 1,6-hexanedithiol (1,6-HDT) in liquid phases on NaA (or 4A-type), CaA (or 5A-type) and NaY zeolites has been studied by using infrared spectroscopy. From the IR spectra it is found that the peak positions of the symmetric as well as the antisymmetric modes of the methylene (CH_2) groups are observed at almost the same band values for the title dithiolates adsorbed on the A-type and NaY zeolites. On the other hand, the weak SH stretching vibration, observed for all samples, can be attributed to the sulphure atoms of 1,5-PDT and 1,6-HDT coordinatively adsorbed on cationic sites of the zeolites.

Key words: Infrared Spectroscopy; Dithiolates; Adsorption; A-types and NaY Zeolites.

1. Introduction

Zeolites have interesting physical and chemical properties. Their catalytic properties are of great practical importance. They can be understood by studying the adsorption characteristics of the reactions on their surfaces [1 – 3]. On the other hand, in the last decade aliphatic as well as aromatic dithiols were of interest due to their remarkable properties (oligomerization, oxidation, multilayer formation) and technical applications (superconductors, pesticides, etc.) [4 – 6]. In particular the adsorption characteristics of aliphatic dithiols on some metals (such as gold and silver) were determined by forming M-S bonds to stabilize higher oxidation states of them and to give high-molecular weight polymers [7]. In this framework, recently the adsorption of 1,5-pentanedithiol (1,5-PDT) and 1,6-hexanedithiol (1,6-HDT) on gold and silver surfaces was studied by using FT-IR spectroscopy and other techniques [8 – 9].

In the present work we describe IR spectral results on 1,5-PDT and 1,6-HDT liquids adsorbed on NaA (4A-type), CaA (5A-type) and NaY zeolites.

2. Experimental

The synthetic zeolites NaA (type 4A), CaA (type 5A) and NaY were purchased from Aldrich Chemical Co. The unit cell of NaA consists of

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O;$$

the zeolite CaA is the calcium-exchanged form of NaA, and the unit cell of NaY consists of

$$Na_{86}(AlO_2)_{56}(SiO_2)_{136}\cdot 250H_2O$$

[10 – 11]. 1,5-Pentanedithiol (Fluka, 95%) and 1,6-hexanedithiol (Fluka, 97%) were used without any purification. The mentioned zeolites were activated at 623 K for 4 h, and then 1 g of each zeolite was placed into 40 ml of each liquid. After stirring and storing for 24 h, the mixtures were filtered, washed twice with ethanol and then filtered again and dried at room temperature.

The samples were compressed to a self-supporting pellet and introduced into an IR cell equipped with KBr windows. The IR measurements at room temperature were performed on a Perkin-Elmer Spectrum One FT-IR (Fourier Transformed Infrared) spectrometer with a resolution of 4 cm^{-1} in the transmission mode.

3. Results and Discussion

The explicit forms of 1,5-pentanedithiol and 1,6-hexanedithiol are $HS(CH_2)_5SH$ and $HS(C_3H_6)_2SH$, respectively. Figures 1a and 1b show the IR spectra of

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Table 1. The IR frequencies (cm^{-1}) of 1,5-PDT adsorbed on CaA, NaA and NaY zeolites.

1,5-PDT	Assignment*	1,5-PDT adsorbed on		
		NaA	CaA	NaY
2928 vs	Asym. CH stretch.	2930 s	2930 s	2931 s
2854 vs	Sym. CH stretch.	2856 s	2855 s	2856 s
2554 s	SH stretch.	2555 m	2555 vw	2554 w
1456 m	CH_2 bending	1457 w	1459 m	1457 m
1432 m	CH_2 bending	1433 w	1423 w	1432sh
1350 m	CH_2 wag.	1367 vw	1383 w	1382 w
1275 s	CH_2 wag.	1274 vw	1278 w	1276 w
1241 s	CH_2 wag.	1241 vw	1240 w	1242 w
1129 m	CH_2 twist	1115 sh	1123 sh	1151 w
1067 w	C–C stretch.	1057 sh	1064 w	–

* Taken from [8, 12]; vs, very strong; s, strong; m, medium; vw, very weak; w, weak; sh, shoulder.

Table 2. IR frequencies (cm^{-1}) of 1,6-HDT adsorbed on CaA, NaA and NaY zeolites.

1,6-HDT	Assignment*	1,6-HDT adsorbed on		
		NaA	CaA	NaY
2927 vs	Asym. CH stretch.	2929 s	2929 s	2929 s
2853 vs	Sym. CH stretch.	2855 s	2854 s	2855 s
2555 s	SH stretch.	2556 m	2555 m	2554 m
1459 m	CH_2 bending	1461 w	1460 m	1460 m
1432 m	CH_2 bending	1433 w	1431 m	1431 w
1351 m	CH_2 wag.	1370 vw	1351 w	1371 w
1269 s	CH_2 wag.	1270 w	1270 m	1267 m
1234 m	CH_2 wag.	–	1233 sh	1231 sh
1124 m	CH_2 twist	1114 sh	1125 sh	1144 m
1071 w	C–C stretch.	1056 sh	1061 sh	–

* Taken from [8, 12]; vs, very strong; s, strong; m, medium; vw, very weak; w, weak; sh, shoulder.

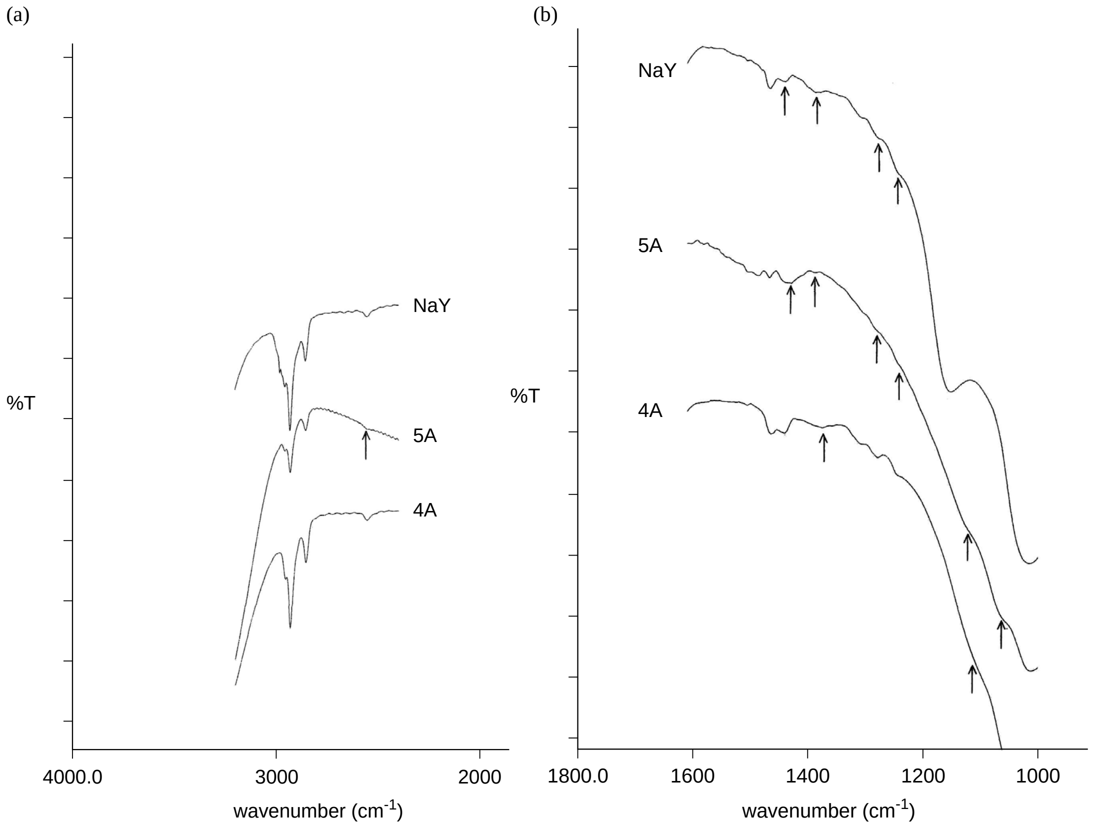

Fig. 1. IR spectra of 1,5-PDT adsorbed on NaA, CaA and NaY zeolites (a) at the interval 2000 – 3250 cm^{-1} and (b) at the interval 1000 – 1600 cm^{-1}.

1,5-PDT adsorbed on NaA, CaA and NaY zeolites, while the IR spectra of 1,6-HDT adsorbed on the mentioned zeolites are shown in Figs. 2a and 2b. The data obtained from the IR spectra of 1,5-PDT and 1,6-HDT, adsorbed on NaA, CaA and NaY zeolites, are summarized in Tables 1 and 2, respectively.

As seen in Tables 1 and 2, there are slight differences between the vibrational bands of 1,5-PDT and 1,6-HDT adsorbed on the mentioned zeolites. For 1,5-PDT, adsorbed on NaA, CaA and NaY zeolites, the ν_{asy}(CH) vibrational bands are observed at 2930 cm^{-1}, 2930 cm^{-1} and 2931 cm^{-1}, and those

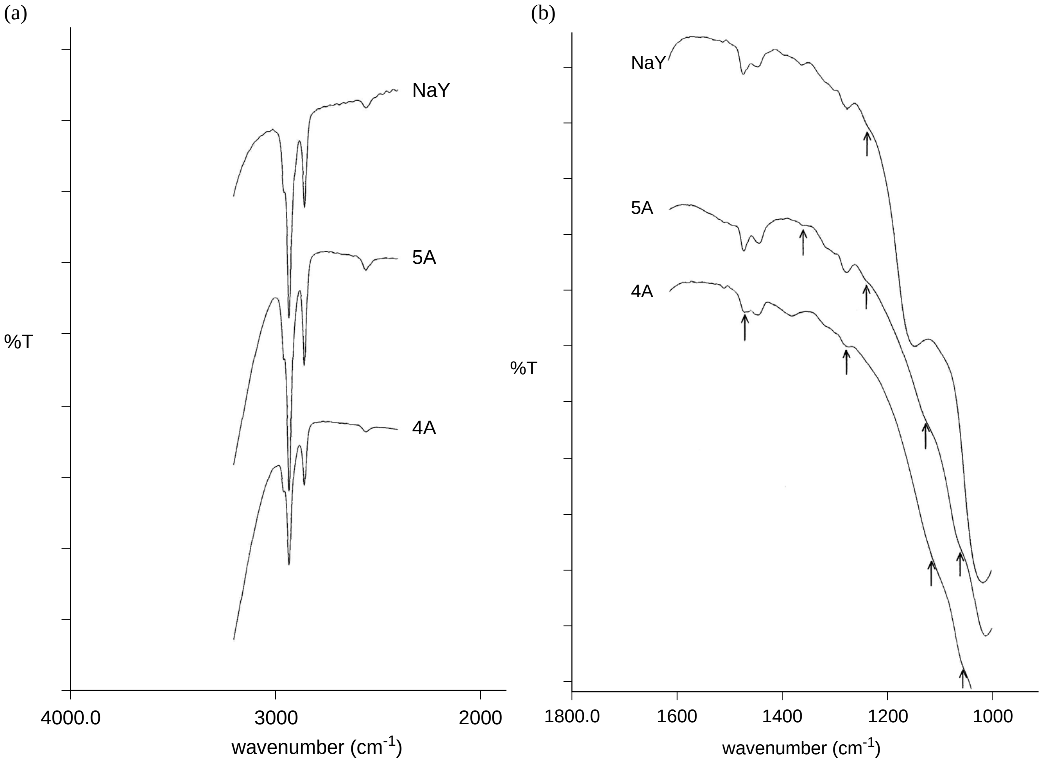

Fig. 2. IR spectra of 1,6-HDT adsorbed on NaA, CaA and NaY zeolites (a) at the interval 2000 – 3250 cm^{-1} and (b) at the interval 1000 – 1600 cm^{-1}.

of the ν_{sym}(CH) vibrational bands at 2856 cm^{-1}, 2855 cm^{-1} and 2856 cm^{-1}, respectively, as seen in Table 1. Similarly for 1,6-HDT adsorbed on the mentioned zeolites, the ν_{asy}(CH) vibrational bands all arised at 2929 cm^{-1}, and the ν_{sym}(CH) stretching bands are observed at 2855 cm^{-1}, 2854 cm^{-1} and 2855 cm^{-1}, respectively. These vibrational frequencies agree very well with the adsorption characteristics of aliphatic dithiols on silver and gold [8]. Then we can state that the ν_{asy}(CH) and ν_{sym}(CH) stretching bands were observed at the same positions in both samples. In other words, the peak positions of stretching modes of the methylene (CH_2) groups of these dithiolates are independent of the structure of the adsorbent surfaces. On the other hand, the SH stretching bands for 1,5-PDT adsorbed on the mentioned zeolites appeared at 2555 cm^{-1}, 2555 cm^{-1} (shown with an arrow on 5A in Fig. 1a) and 2554 cm^{-1}, respectively. The same SH weak band for 1,6-HDT adsorbed on the 4A, 5A and NaY zeolites are clearly observed at 2556 cm^{-1}, 2555 cm^{-1} and 2554 cm^{-1}, respectively, as seen in Figure 2a. In fact, the SH stretching bands in zeolitic catalysts were usually attributed to the SiOHAl (Brönsted acid sites) and the cationic (Na^+) sites [13 – 14]. For our samples these weak SH stretching bands can be assigned to the cationic sites of the mentioned zeolites by considering the adsorption charactreristics of dithiolates which form M-S bonds as depicted in Fig. 3 [8, 13].

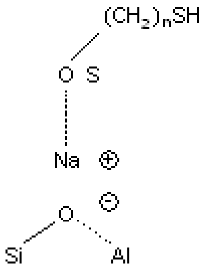

Fig. 3. A model for the adsorbed dithiolates on cationic sites of the mentioned zeolites.

In Fig. 1b the methylene wagging band at 1367 cm^{-1} and the methylene twisting band at 1115 cm^{-1} for 1,5-PDT adsorbed on 4A zeolite are denoted with the arrows. Similarly, for 1,5-PDT asorbed on 5A and NaY zeolites the bending, wagging and twisting vibrational modes of the methylene groups are shown with arrows as seen in Figure 1b. Furthermore the CC stretching vibrational mode at 1725 cm^{-1} for adsorbed 1,5-PDT on CaA zeolite is denoted with an arrow in Figure 1b. In a similar way the arrows seen in Fig. 2b, which containes the frequency region between 1000 – 1600 cm^{-1} for adsorbed 1,6-HDT on the mentioned zeolites, show the bands above, and they can be explained by considering Table 2.

In conclusion, for systems which include the adsorbate and zeolites as adsorbent, the bridging hydroxyl groups at Brönsted acid sites and non-acidic silanol hydroxyls at the surfaces of zeolites are considered as sources of adsorptions. Previous works, done by Joo and coworkers and others, for dithiols adsorbed on gold and silver surfaces indicate that their adsorption characteristics were identified by considering the CH and SH stretching vibrational modes. Our results obtained from IR spectra of 1,5-PDT and 1,6-HDT adsorbed on NaA, CaA and NaY zeolites agree very well with those of them.

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