FT-IR Spectroscopic Study of 1,3-Diaminopropane Adsorbed on Type A, X and Y Zeolites

Nuri Öztürk and Semiha Bahçeli

Department of Physics, Faculty of Arts and Sciences, Süleyman Demirel University, 32260 Isparta, Turkey

Reprint requests to Prof. S. B; E-mail: bahceli@fef.sdu.edu.tr

Z. Naturforsch. **61a,** 399 – 401 (2006); received May 15, 2006

The IR spectra of 1,3-diaminopropane adsorbed on NaA (type 4A), CaA (type 5A), NaX (type 13X) and NaY zeolites are reported. From the IR spectral data it can easily be stated that the characteristic NH vibration bands of aliphatic amine groups play an important role in the adsorptions of 1,3-diaminopropane on the mentioned zeolites.

Key words: Infrared Spectroscopy; 1,3-Diaminopropane; Zeolites; Adsorption.

1. Introduction

Zeolites are the best known microporous molecular sieves and adsorbe molecules below a particular size in their pore structures. Therefore they are considered as heterogenous catalysts and sorbents [1]. The catalytic properties of zeolites can be understood by investigating the adsorption characteristics of reactions on their surfaces [2, 3]. During the past years the adsorption of some compounds which include amine groups have been studied by using infared spectroscopy [4]. Very recently, the adsorption of 1,3-diaminopropane which contains primary aliphatic amine groups on calix[4]arene has been studied by using FT-IR (Fourier Transform Infrared) [5].

The purpose of the present work is to offer the IR spectra of 1,3-diaminopropane adsorbed on NaA, CaA, NaX and NaY zeolites in which the more small cavities relative to calix[4]arenes are formed.

2. Experimental

All synthetic zeolites, NaA (type 4A, Aldrich), CaA (type 5A, Aldrich), NaX (type 13X, Fluka) and NaY (Aldrich), were obtained from commercial sources. The unit cell of zeolites NaA and CaA consists of

$$M[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O,$$

where M = Na and Ca, respectively, while the unit cells of the zeolites NaX and NaY consist of

$$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot 264H_2O$$

and

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

[6, 7]. The liquid 1,3-diaminopropane (Acros, 99%) was used without purification. First, the mentioned zeolites were activated at 623 K for 4 h, and then 1 g of each zeolite was placed into 40 ml of 1,3-diaminopropane. 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 into self-supporting pellets and introduced into an IR cell equipped with KBr windows. IR measurements at room temperature

Table 1. The IR frequencies (cm^{-1}) of bulk 1,3-diaminopropane (1,3-DAP) and adsorbed 1,3-diaminopropane on NaA, CaA, NaX and NaY zeolites.

1,3-DAP	Assignment	Frequencies of 1,3-DAP adsorbed on			
		NaA	CaA	NaX	NaY
3357 s	ν_{as}(NH)	–	3310 sh	–	–
3279 s	ν_s(NH)	3232 sh	–	3273 sh	3273 sh
2923 s	$\nu_{as}(CH_2)$	2939 sh	2943 m	–	2934 w
2846 s	$\nu_s(CH_2)$	–	2877 vw	2877 sh	2881 sh
1599 vs	NH bend. (scis.)	1571 s	1601 m	1581 s	1579 m
1470 s	CH_2 scissoring	1491 m	1483 s	1490 s	1492 m
1433 s	CH_2 scissoring	1437 m	1436 m	1436 m	1436 m
1388 s	CH_2 scissoring	1387 bm	1401 m	1387 w	1384 w
1315 m	CH_2 twist.	1329 s	1328 s	1335 s	1329 s
1068 m	ν(CN)	1054 sh	1059 sh	1061 vw	–
834 bm	NH wagging	823 w	824 m	824 m	819 vw
767 w	NH wagging	754 sh	756 sh	–	768 sh

v, very; s, strong; m, medium; bm, broad medium; w, weak; bsh, broad shoulder; sh, shoulder; ν, stretching.

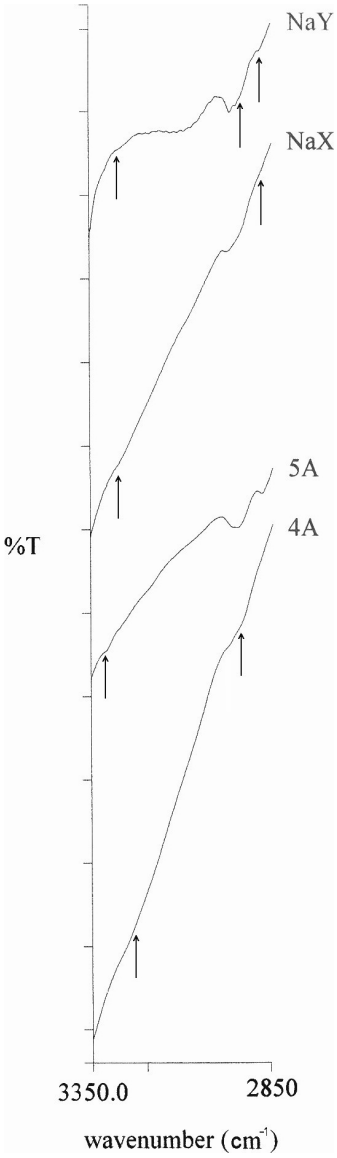

Fig. 1. Infrared spectra of adsorbed 1,3-DAP on NaA (type 4A), CaA (type 5A), NaX and NaY zeolites in the interval 3350 – 2850 cm^{-1}.

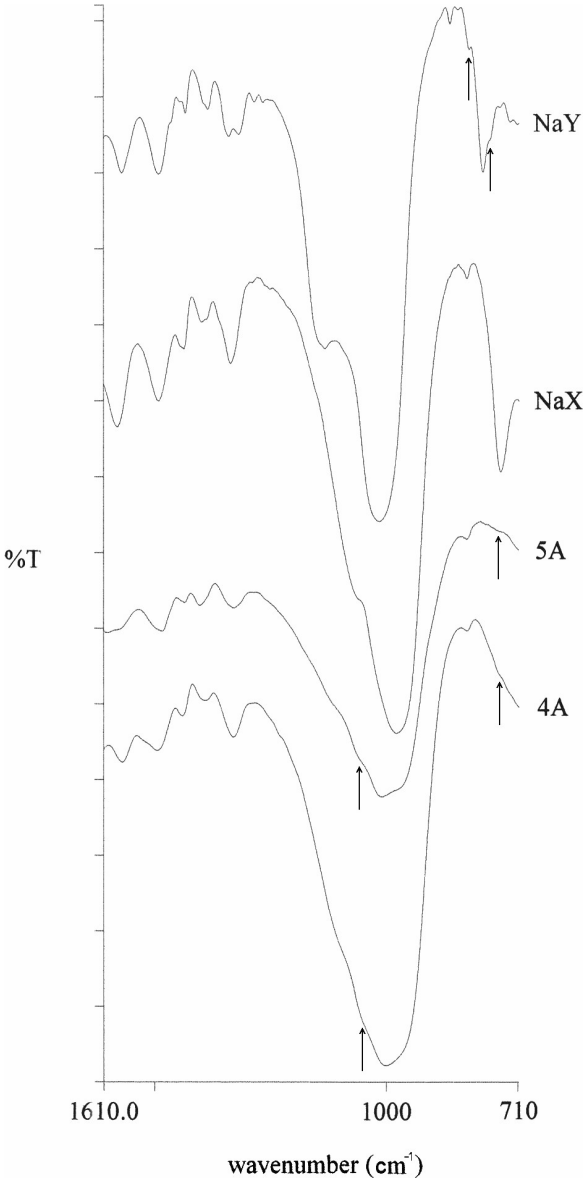

Fig. 2. Infrared spectra of adsorbed 1,3-DAP on NaA (type 4A), CaA (type 5A), NaX and NaY zeolites in the interval 1610 – 710 cm^{-1}.

were performed on a Perkin-Elmer Spectrum One FT-IR spectrometer with a resolution of 4 cm^{-1} in the transmission mode.

3. Results and Discussion

The explicit formula of 1,3-diaminopropane (1,3-propanediamine, 1,3-DAP) is $C_3H_{10}N_2$. The IR spectra of 1,3-diaminopropane adsorbed on synthetic zeolites NaA (type 4A), CaA (type 5A), NaX (type 13X) and NaY are given for two frequency ranges in Figs. 1 (3350 – 2850 cm^{-1}) and 2 (1610 – 710 cm^{-1}). The data obtained from IR spectra are summarized in Table 1.

For the assignments of IR vibrational frequencies of bulk 1,3-DAP in Table 1 we referred to [5, 8 – 10]. As seen in Table 1 and Fig. 1, the asymmetric NH stretching vibration band of bulk 1,3-DAP at 3357 cm^{-1} is observed as a shoulder band at 3310 cm^{-1} for 1,3-DAP absorbed on the zeolite CaA. But the symmetric NH

stretching mode of liquid 1,3-DAP at 3279 cm^{-1} appears as the shoulder bands at 3232 cm^{-1}, 3273 cm^{-1} and 3273 cm^{-1} for adsorbed 1,3-DAP on NaA, NaX and NaY zeolites, respectively. They are indicated with arrows in Figure 1. On the other hand the asymmetric vibrational CH_2 stretching bands of adsorbed 1,3-DAP on NaA, CaA and NaY zeolites can be attributed to the bands at 2939 cm^{-1} (shown with an arrow in Fig. 1), 2943 cm^{-1} and 2934 cm^{-1} (shown with an arrow in Fig. 1), respectively. Similarly, the symmetric vibrational CH_2 stretching bands of adsorbed 1,3-DAP on CaA, NaX and NaY zeolites take place in the higher frequency region at 2877 cm^{-1}, 2877 cm^{-1} (shown with an arrow in Fig. 1) and 2881 cm^{-1} (shown with an arrow in Fig. 1), respectively. As for Fig. 2 the vibrational CN stretching at 1068 cm^{-1} for bulk 1,3-DAP is shifted to the shoulder bands at 1054 cm^{-1} and 1059 cm^{-1} (which are shown with arrows in Fig. 2 for adsorbed 1,3-DAP on NaA and CaA zeolites), respectively, in the lower frequency region. In this framework the vibrational NH wagging at 834 cm^{-1} for liquid 1,3-DAP is slightly shifted to lower frequencies for adsorbed 1,3-DAP on the mentioned zeolites (the band at 819 cm^{-1} for adsorbed 1,3-DAP on NaY is shown with an arrow in Fig. 2). Furthermore, the NH wagging vibrational bands of adsorbed 1,3-DAP on NaA and CaA zeolites are shown with arrows in Fig. 2 at 754 cm^{-1} and 756 cm^{-1}, respectively. As seen in Table 1 and Fig. 2, the NH bending vibration of the aliphatic amine group produce a band in the interval 1571 – 1601 cm^{-1} for all samples, and it can be estimated to be adsorbed as surface amine ions. The suggestion by Mortland et al. states that the structural hydroxy groups in zeolites were relatively inactive at room temperatures [11]. On the other hand the remaining silanol hydroxy groups on the surfaces of zeolites can interact by hydrogen bonding with methylene groups of adsorbed 1,3-DAP molecules [12].

As a conclusion it can be declared that the sources of adsorptions of bulk 1,3-diaminopropane on NaA, CaA, NaX and NaY zeolites seem to be the interactions between the silanol hydroxy groups on the surface of zeolites and both aliphatic amine and methylene groups of the 1,3-DAP molecule.

Acknowledgements

This work was supported by the Unit of the Management of Scientifical Research Projects within the project No. 984-m-05 of the Süleyman Demirel University.

[1] R. M. Barrer, Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, London 1978.
[2] J. Klinowski, Anal. Chim. Acta **283**, 929 (1993).
[3] N. Öztürk, Ç. Çırak, and S. Bahçeli, Z. Naturforsch. **60a**, 633 (2005).
[4] L. H. Little, A. V. Kiselev, and V. I. Lygin, Infrared Spectra of Adsorbed Species, Academic Press, London 1966, pp. 193 – 247.
[5] T. Tilki, N. Öztürk, and S. Bahçeli, to be published.
[6] F. A. Mumton, Mineral Soc. Am. Course Notes **4**, 221 (1977).
[7] J. Scott, Zeolite Technology and Applications: Recent Advances, Noyes Data Corporation, Park Ridge, NJ 1980, p. 30.
[8] R. M. Silverstein and F. X. Webster, Spectroscopic Identification of Organic Compounds, John Wiley and Sons, New York 1998, p. 102.
[9] N. B. Colthup, L. H. Dally, and S. E. Wimberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York 1964, Chapter 11, p. 278.
[10] L. J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen and Co., London 1962, Chapter 14, p. 284.
[11] M. M. Mortland, J. J. Fripiat, J. Chaussidon, and J. Uytthoeven, J. Phys. Chem. **67**, 248 (1963).
[12] R. S. MacDonald, J. Phys. Chem. **62**, 1168 (1958).