

FT-IR Spectroscopic Study of Triethyl Phosphate Adsorption on FAU Type Zeolite

BELGİN BARDAKÇI* and NESLİHAN KAYA†
*Department of Physics, Faculty of Arts and Sciences,
Mehmet Akif Ersoy University, Burdur, Turkey
Fax: (90)(248)2122781; Tel: (90)(248)2122780-1681
E-mail: bbardakci@mehmetakif.edu.tr*

The adsorption of triethyl phosphate on FAU type zeolite has been investigated by using FT-IR spectroscopy. Zeolites are a large and diverse class of volcanic aluminosilicate crystalline materials which have many useful applications. They are used in oil cracking, adsorption of nuclear waste as well as production of controlled-release fertilizers for agriculture, adsorption of ammonia and other odour-volatiles, as cation absorbers in household detergents, as molecular sieves and for many other uses. Zeolites, which are known by their porous structure, are used widely to remove pollutants from nature. In this point of view, zeolites are special type of mineral which is playing an increasing role to solve environmental problems. In this study, we used NaY and NaX zeolites as adsorbents. After adsorption process, characteristic wavenumbers of triethyl phosphate had been observed by FT-IR spectroscopy. Addition to that, elemental analysis results had been supported that adsorption occurred on zeolite surface.

Key Words: Zeolite, FAU type, FTIR, Adsorption.

INTRODUCTION

Zeolites are microporous crystalline solids with well-defined structures and the primary structural units of zeolites are the tetrahedra of silicon and aluminum SiO_4 and AlO_4 ¹. When a zeolite framework contains an equal number of aluminum and silicon atoms, each oxygen atom is linked to one aluminum atom and to one silicon atom and the cavities contain the maximum density of exchangeable cations². Synthetic zeolites with such a maximum cation exchange capacity are of interest as ion exchangers and adsorbents. A zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniformly sized pores of molecular dimensions. As the pores preferentially adsorb molecules that fit snugly inside the pores and exclude molecules that are too large, they act as sieves on a molecular scale. Thus, zeolites are a subset of molecular sieves³. The use of molecular sieves

†Experimental and Observational Research and Application Centre, Süleyman Demirel University, West Campus, Isparta, Turkey.

with three-dimensional framework structures is well entrenched in areas as diverse as laundry detergents, oil refining and petrochemical industries, adsorbents, gas separations, agriculture and horticulture, pigments and jewelry^{3,4}. In this work, the absorption of triethyl phosphate (TEP) (Fig. 1) on the NaX and NaY zeolites has been studied by using infrared spectroscopy. Using of results is purposed in nature and agriculture pollution.

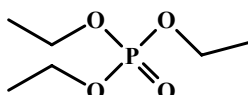


Fig. 1. Molecular structure of triethyl phosphate (TEP)

European directives, manufacturers are now required to massively cut down the phosphorus content by chemical means in their water treatment plants. Triethyl phosphate comes out as a by-product of agricultural pesticides. In most of the pesticides, triethyl phosphate remains, must be removed from nature, which will eliminate a long standing problem that agriculture faces and help to prevent environmental pollution.

FTIR spectroscopy can be used not only for the identification of a functional group but also for the investigation of the chemical band. In addition, infrared spectroscopy contributes considerably for structure analysis of an unknown sample. In this study, adsorption region can be easily determined by using IR spectroscopy^{5,6}.

EXPERIMENTAL

The synthetic zeolites types NaX and NaY were purchased from Sigma-Aldrich Chemical Company. Unit cell structure of NaX and NaY zeolites are $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}].264\text{H}_2\text{O}$ and $\text{Na}_{56}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}].250\text{H}_2\text{O}$, respectively.

The liquid triethyl phosphate (Aldrich 98 %) was used without purification, first the IR spectrum of bulk 1-TEP was obtained and then NaX and NaY zeolites activated at 673 K for 4 h. Then, for TEP adsorption 1 g of the each zeolite was placed into 20 cm³ of liquid TEP. After stirring and storing for 48 h, the mixture was filtered and dried at room temperature.

Then, the suspension was filtered The Millipore purified (18.2 mΩ cm) water was used in all experiments. For adsorption process, we used the method which had been performed before⁷. The samples were slowly dried in air and mixed (1.0 %) with KBr and pressed into pellets. The prepared samples were characterized by infrared spectroscopy using a Perkin-Elmer FTIR spectrum BX II spectrometer. For the IR spectrum of bulk TEP, ATR (attenuated total reflectance) equipment which is made of ZnSe was used. The adsorption of TEP on NaX and NaY zeolites samples was monitored by infrared spectroscopy. Elemental analysis has been known as important process of accurately determining the composition of elements in materials. The most common form of elemental analysis, C analysis, is accomplished by. In

this technique, a sample is burned in an excess of oxygen and various traps collect the combustion products carbon dioxide. The weights of these combustion products can be used to calculate the composition of the unknown sample. The prepared compounds were analyzed by using a LECO CHNS 932 model analyzer for carbon.

RESULTS AND DISCUSSION

IR spectra of the bulk TEP are given in Fig. 2. IR spectra of TEP adsorbed on the NaX zeolite and NaY zeolite are given in Fig. 3(a-b). IR spectral data for each sample with adsorbed TEP listed in Table-1.

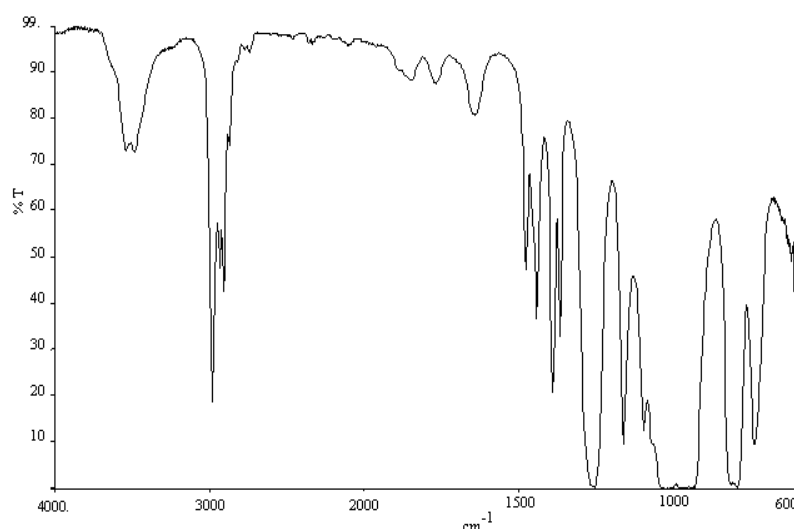


Fig. 2. FTIR-ATR spectrum of the bulk TEP

The strong band⁸ at 2982 cm^{-1} and the medium band⁹ at 2908 cm^{-1} are assigned to C-H symmetric stretching mode of TEP. The bands of TEP adsorbed on NaX and NaY zeolites are observed as medium band^{10,11} at 2986, 2987 and 2912 cm^{-1} in higher frequency region, respectively. In Table-2, the C-H asymmetric vibration mode at 2933¹⁰ cm^{-1} and 2971¹¹ cm^{-1} for bulk triethyl phosphate are observed in the IR spectra of adsorbed TEP on NaX and NaY zeolites as weak band at 2935, 2937 and 2872, 2873 cm^{-1} , respectively.

Characteristic vibration bands of bulk TEP are $\nu_s(\text{P}=\text{O})$ and $\nu_{as}(\text{PO}_3)$ stretching bands at 1259¹⁰ cm^{-1} and 1165¹¹ cm^{-1} . The band of TEP adsorbed on FAU-type zeolites are observed as medium bands at 1262 and 1263 cm^{-1} , in the higher frequency region and as weak bands 1166 and 1165 cm^{-1} , respectively.

The weak band at 1099^{12,13} cm^{-1} is assigned to O-P-O stretching mode of TEP. The band of TEP adsorbed on NaY zeolite is observed as weak band at 1102 cm^{-1} in higher frequency region. The weak band at 817¹⁰ cm^{-1} is assignment to (P-O)-C stretching mode of TEP. The band of TEP adsorbed on NaX and NaY zeolites are observed as medium band at 822 cm^{-1} and as weak band 824 cm^{-1} in higher frequency

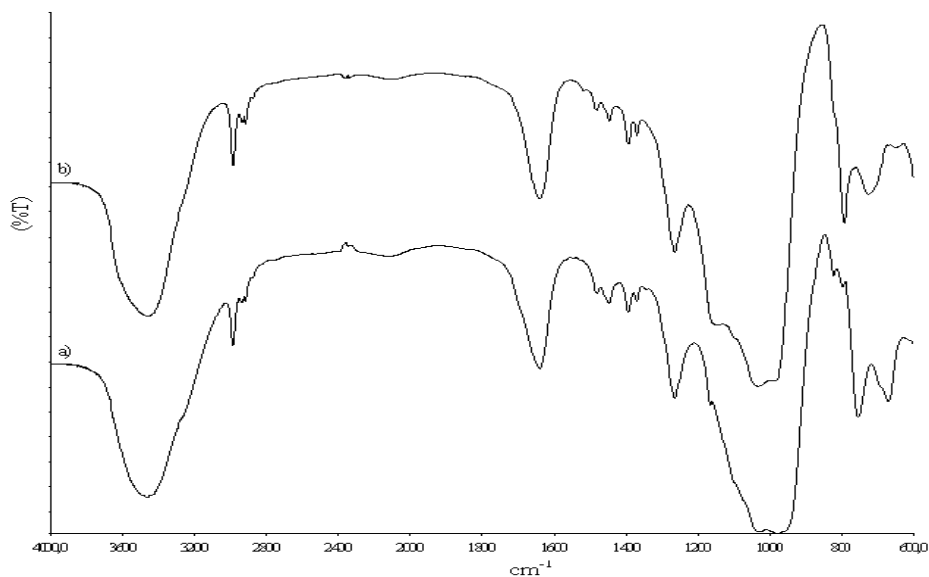


Fig. 3. IR spectra of TEP adsorbed on the (a) NaX zeolite and (b) NaY zeolite

TABLE-1
IR FREQUENCIES (cm^{-1}) OF LIQUID TEP AND ADSORBED
TEP ON NaX AND NaY ZEOLITES

Bulk TEP	Assignment	Frequency adsorbed on	
		NaX	NaY
2982 s	ν_{sCH}	2986 m	2987 m
2933 m	ν_{asCH}	2935 w	2937 w
2908 m	ν_{sCH}	2912 w	2912 w
2871 w	ν_{asCH}	2872 w	2873 w
1479 m	ν_{CH}	1480 w	1480 w
1444 s	$\delta_{\text{CH}}(\text{CH}_3)$	1445 w	1446 w
1392 s	$\delta_{\text{CH}}(\text{CH}_3)$	1394 w	1395 w
1368 s	$\delta_{\text{CH}}(\text{CH}_3)$	1370 w	1370 w
1259 b	$\nu_{\text{PO}}(\text{P=O})$	1262 m	1263 m
1165 s	ν_{PO}	1166	1165w
1099 w	ν_{PO}	1102 w	—
817 w	$\nu_{\text{PO}}(\text{P-O-C})$	822	824 w
796 w	ν_{PO}	794 m	799 w
743 s	γ_{CH}	724 m	752 m

TABLE-2
ELEMENTAL ANALYSIS RESULTS FOR ADSORBED
TEP ON NaX AND NaY ZEOLITES

Adsorbed TEP	Quantitative mass % C
NaX	11.33
NaY	10.92

region, respectively. On the other hand, The P-O-P stretching vibration band at 796^{10} cm^{-1} for bulk TEP is observed as medium band at 794 cm^{-1} weak band at 799 cm^{-1} for TEP adsorbed on NaX and NaY zeolites, respectively. The medium band at 1479^{12} cm^{-1} is assigned to C-H symmetric stretching mode of bulk TEP. The symmetric stretching band of C-H is 1480 cm^{-1} for TEP adsorbed on NaX and NaY zeolites. The vibration band of bulk TEP is $\delta(\text{CH}_3)$ out-of-plane¹³ at 1444 , 1392 and 1368 cm^{-1} . The bands of TEP adsorbed on NaX and NaY zeolites are observed as weak bands 1445 and 1446 cm^{-1} , 1394 and 1395 cm^{-1} , 1370 cm^{-1} in higher frequency region. On the other hand, The C-H out-of-plane vibration band^{12,14} at 743 cm^{-1} for bulk TEP is observed as medium bands at 724 and 752 cm^{-1} for TEP adsorbed on NaX and NaY zeolites, respectively.

Conclusion

It is concluded that vibrational bands of FTIR spectra after adsorption process of TEP on FAU type zeolites, specially availability of C-H bands and P=O band indicated adsorption process was performed well on mentioned zeolites. Results of elemental analysis after adsorption process agree well with FTIR results.

ACKNOWLEDGEMENT

This project was supported by Mehmet Akif Ersoy University, The Unit of the Management of Scientific Research Projects within the project No. 12-NAP-07.

REFERENCES

1. A. Dyer, *An Introduction to Zeolite Molecular Sieves*, John Wiley and Sons (1988).
2. D.W. Breck, *Zeolite Molecular Sieves*, Robert E. Krieger Company Malabar, Florida (1984).
3. J. Cezka, H. Bekkum, A. Corma and F. Schüth, *Introduction to Zeolite Science and Practice*, 3rd Revised Edition Elsevier B.V., pp. 1-9 (2007).
4. A.A. Isildar, *Tr. J. Agric. Forest.*, **23**, 363 (1999).
5. A.A. Christy, Y. Ozaki and V.G. Gregoriou, *Modern Fourier Transform Infrared Spectroscopy*, Elsevier Science (2001).
6. J.A. Rabo, *Zeolite Chemistry and Catalysis*, American Chemical Society, Washington DC (1976).
7. B. Bardakçi and S. Bahçeli, *Z. Naturforsch. A*, **60a**, 637 (2005).
8. M.S. Saraiva, N.L. Dias Filho, C.D. Nunes, P.D. Vaz, T.G. Nunes and M.J. Calhorda, *Micropor. Mesopor. Mater.*, **117**, 670 (2009).
9. A.G. Baddi, M. Hafidi, V. Gilard and J.-C. Revel, *Agronomie*, **23**, 661 (2003).
10. V. Vidya, K. Sankaran, K. Sundararajan and K.S. Viswanathan, *J. Molecular Struct.*, **476**, 97 (1999).
11. M. Sherief, N.A. Ghoneim and H.A. El-Batal, *J. Mater. Sci.: Mater. Electronics*, **15**, 273 (2004).
12. I. Poljansek and M. Krajnc, *Acta Chim. Slov.*, **52**, 238 (2005).
13. B. Smith, *Infrared Spectral Interpretation*, CRC Press, Boca Raton, pp. 1-265 (1999).
14. M.S.U. Kalsom, H. Nur, A.A. Norlea and S. Ngaspan, *J. Trop. Agric. Fd. Sc.*, **34**, 165 (2006).