

Spectroscopic Studies of 5-*o*-Tolyl-2-pentene Adsorbed on 5A, NaY and NaX Zeolites

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The adsorption of 5-*o*-tolyl-2-pentene in liquid phase on 5A, NaY and NaX zeolites has been studied by IR spectroscopy. The slightly higher preference of Na cation-exchanged zeolites for an alkene can be clarified in term of stronger interaction of unsaturated hydrocarbons with ionic nature of the zeolite surface. The IR results show that methyl and methylene groups are the sources of adsorption on cationic site of the zeolites.

Key Words: FTIR, Adsorption, 5-*o*-Tolyl-2-pentene, Zeolite.

INTRODUCTION

It is well known that the infrared spectroscopy is one of the most powerful methods for investigation of zeolites which have the cage structure. Zeolites have a number of interesting physical and chemical properties. The three properties which are of greatest practical importance are the ability of to absorb organic and inorganic substances, to act as cation exchangers and to catalyze a wide variety of reactions. The catalytic properties of zeolites can be understood by studying the adsorption characteristic of molecules accumulated on their surface using IR spectroscopy^{1,2}. In literature, *o*-xylene with 1,3-butadiene were used for the synthesis of 5-*o*-tolyl-2-pentene (OTP) by means of an alkenylation reaction³⁻⁵. The aim of the present work is to explain IR spectral results of OTP adsorption on 5A, NaY and NaX zeolites.

EXPERIMENTAL

The synthetic zeolites type 5A, NaX (type 13X) and NaY were purchased from Sigma-Aldrich Chemical Company. 5A Zeolite is calcium-exchanged form of 4A zeolite. The unit cell of 5A consists of $M[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$, $M = Na$ and Ca ^{6,7}, while the unit cells of zeolites NaY and NaX consist of $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250H_2O$ and $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264H_2O$, respectively⁷.

The liquid OTP (Aldrich 98 %) was used without purification, first the IR spectrum of bulk OTP was obtained and then each type of zeolites activated 673 K for 4 h. Adsorption process of OTP was performed on mentioned zeolites. Adsorption process

explained in details in another⁸. Only mixture samples were compressed to a self supporting pellet and introduced to IR cell equipped with KBr windows. For the IR spectrum of bulk OTP, ATR (attenuated total reflectance) equipment which is made of ZnSe was used. The all IR measurements were performed on a Perkin-Elmer spectrum BX FT-IR (fourier transform infrared) spectrometer with a resolution of 4 cm^{-1} in the transmission mode, at room temperature.

RESULTS AND DISCUSSION

The chemical formula of 5-*o*-tolyl-2-pentene (OTP) is $\text{CH}_3\text{C}_6\text{H}_4(\text{CH}_2)_2\text{CH}=\text{CHCH}_3$. Due to absence of vibrational frequencies of OTP, the IR spectral data of this chemical were needed for assignments. In Fig. 1, the spectrum of OTP is shown.

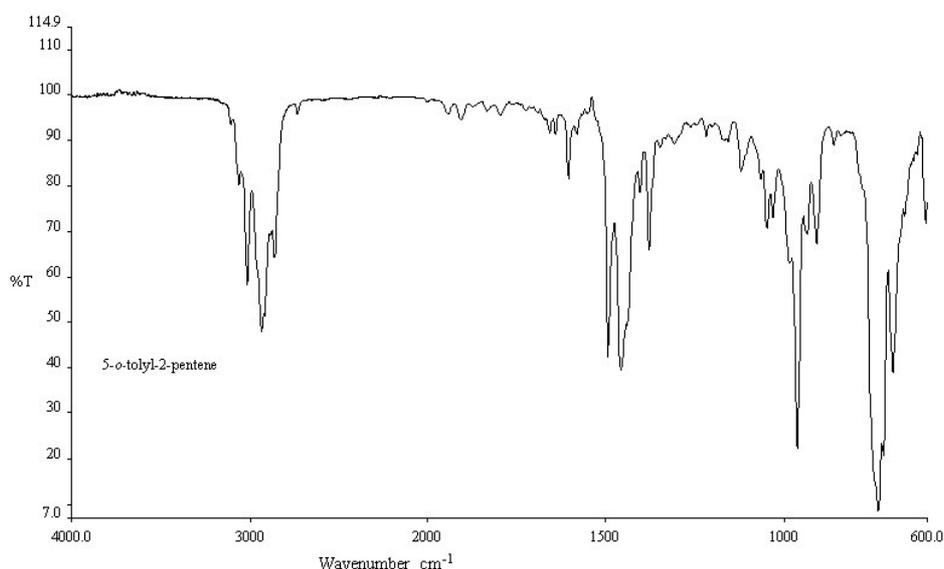


Fig. 1. IR spectrum of bulk 5-*o*-tolyl-2-pentene (OTP)

Figs. 2a-c show the IR spectra of OTP adsorbed on 5A, NaY and NaX zeolites, respectively. The arrows in figures show weak or shoulder bands.

The data obtained from IR spectra of OTP adsorbed on 5A, NaY and NaX zeolites and as well as the IR spectrum of bulk OTP are summarized in Table-1.

It is stated before that, if the C-H bond is adjacent to a double bond or aromatic ring, the C-H stretching wavenumber absorbs⁹ between 3100 and 3000 cm^{-1} . As seen in Fig. 1 and Table-1, C-H stretching vibration bands of bulk OTP are observed as a weak band at 3062 cm^{-1} and and a strong band at 3014 cm^{-1} . After adsorption of OTP on mentioned zeolites, these two bands are shifted to 3065 and 3017 cm^{-1} for 5A zeolite and for NaY and NaX zeolites these two bands can be observed at 3064 and 3016 cm^{-1} . Intensity of each peak of bulk OTP is relative to

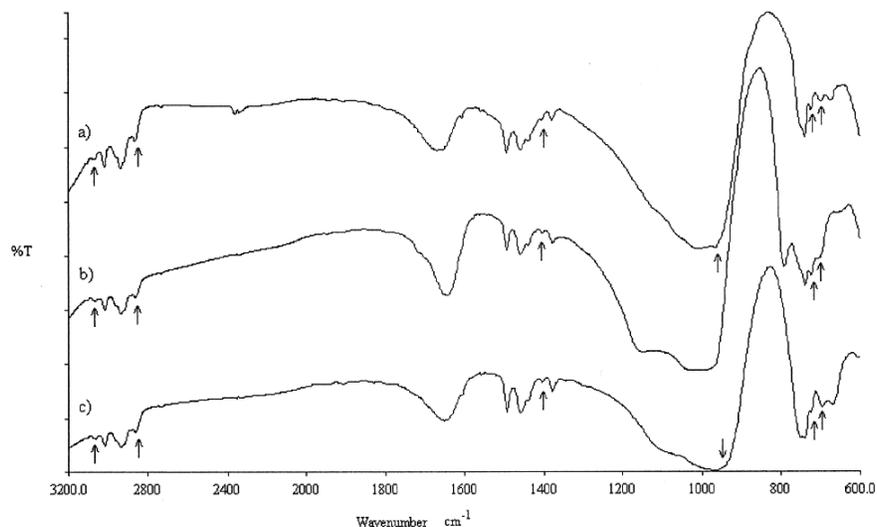


Fig. 2. IR spectra of OTP adsorbed on a) 5A b) NaY and c) NaX zeolites

TABLE-1
IR FREQUENCIES (cm^{-1}) OF OTP ADSORBED ON CaA, NaY, NaX
ZEOLITES, BULK OTP AND ASSIGNMENT

Assignment	5- <i>o</i> -Tolyl-2-pentene	5- <i>o</i> -Tolyl-2-pentene adsorbed on zeolites		
		5A	NaY	NaX
C-H str	3062 w	3065 sh	3064 w	3064 w
C-H str	3014 s	3017 m	3016 m	3016 m
$\nu_{\text{as}}(\text{CH}_2)$	2934 s	2937 m	2936 m	2936 m
$\nu_{\text{s}}(\text{CH}_2)$	2863 m	2865 w	2864 w	2864 w
Ring mode	1492 s	1493 m	1493 m	1493 m
$\delta_{\text{as}}(\text{CH}_3), \delta_{\text{s}}(\text{CH}_2)$	1457 s	1458 m	1458 m	1458 m
$\beta(\text{C-H})$	1402 m	1403 sh	1403 sh	1403 w
$\delta_{\text{s}}(\text{CH}_3)$	1377 s	1378 w	1377 w	1378 w
$\gamma(\text{C-H})$	964 s	966 sh	–	966 sh
$\gamma(\text{C-H})_{\text{ar}}$	737 s	738 m	738 m	740 m
$\rho(\text{CH}_2)$	722 s	723 w	723 w	724 sh
Ring bending C-C	696 s	698 w	699 sh	695 w

ν = stretching; δ = deformation (bending); β = bending in-plane; γ = bending out-of-plane;
 ρ = rocking; str = stretching as = asymmetric; s = symmetric; ar = aromatic; s = strong;
 m = medium; w = weak; sh = shoulder.

samples of which OTP adsorbed on zeolites. The asymmetric vibration CH_2 stretching bands of adsorbed OTP on 5A, NaY and NaX zeolites can be attributed to the bands at 2937, 2936 and 2936 cm^{-1} , respectively. In addition to that, the symmetric vibration CH_2 stretching bands of adsorbed OTP on 5A, NaY and NaX zeolites appear as weak bands at 2865 and 2864 cm^{-1} , respectively. The strong band at 1492 cm^{-1} of

OTP can be attributed to ring breathing mode¹⁰ which is shifted to 1493 cm⁻¹ for all zeolites. The prominent band at 1457 cm⁻¹ of OTP can be assigned to either asymmetric methyl deformation or symmetric methylene deformation band¹¹. The less intense band located at 1402 cm⁻¹ could be associated to the in plane C-H bending vibrations of the benzene ring that interacts (sometimes strongly) with various ring C-C vibrations¹² and this band was observed as a shoulder band at 1403 cm⁻¹ on mentioned zeolites. The band at 1377 cm⁻¹ of bulk OTP spectrum arising from the symmetrical bending of methyl C-H bonds¹³. This band is shifted to 1378 cm⁻¹ for 5A and NaX zeolites. It is noted that all C-H vibration (whether belong to CH₂ or CH₃) bands were observed in the same position for all samples. A strong band at 737 cm⁻¹ can be assigned to aromatic C-H bond, as it was declared before by other scientists¹⁴. This peak at 737 cm⁻¹ of OTP shifted to a band at 738 cm⁻¹ of adsorbed OTP on 5A and NaY zeolite and 740 cm⁻¹ for NaX zeolite. The peak at 964 cm⁻¹ is attributed to out of plane C-H bending of OTP¹⁰. Although this band cannot be observed on NaY zeolite, it is observed at 966 cm⁻¹ as a shoulder band in OTP adsorbed on 5A and NaX zeolites. The strong peak of 722 cm⁻¹ is ascribed to the rocking vibration of methylene group.

Conclusion

Na⁺ cation is a common property of all the three zeolites. The slightly higher preference of Na cation-exchanged zeolites for an alkene can be clarified in term of stronger interaction of unsaturated hydrocarbons with ionic nature of the zeolite surface¹⁵. Hydrocarbon molecules with double bonds are strongly sorbed and the π -electrons may probably interact with cation sites of zeolite, as it was shown before in NaY zeolite¹⁶. Silanol hydroxyl groups on the surface of zeolites can interact by hydrogen bonding with methylene and methyl groups of OTP. As a conclusion, it can be stated that, methyl and methylene groups of OTP are the source of adsorption on cationic site of all the three zeolites.

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REFERENCES

1. J.M. Chalmers and P.R. Griffiths, Handbook of Vibrational Spectroscopy, Chichester, UK, Wiley, pp. 3042-3071 (2002).
2. H. Con, S.I. Woo and S.-E. Park, Recent Advances and New Horizons in Zeolite Science and Technology, Amsterdam, Elsevier Science B.V., pp. 97-139 (1996).
3. L. Wang and J. Zhen, *Ultrason. Sonochem.*, **13**, 215 (2006).
4. E.J. Dorskocil, S.V. Bordawekar and R.J. Davis, Catalysis by Solid Bases, Cambridge, UK Catalysis, The Royal Society of Chemistry, pp. 40-72 (2000).
5. E.J. Dorskocil and R.J. Davis, *J. Catal.*, **188**, 353 (1999).
6. A. Dyer, An Introduction to Zeolite Molecular Sieves, Chichester, John Wiley & Sons, p. 149 (1988).

7. J.A. Rabo, Zeolite Chemistry and Catalysis, Washington DC, America Chemical Society, pp. 3-79 (1976).
8. B. Bardakçi and S. Bahçeli, *Z. Naturforsch A*, **60**, 637 (2005).
9. B. Stuart, Infrared Spectroscopy: Fundamentals and Application, NJ, USA, John Wiley & Sons, Hoboken, p. 47 (2004).
10. B. Smith, Infrared Spectral Interpretation, A Systematic Approach, Boca Raton London, CRC Press LLC, p. 265 (1999).
11. N.B. Colthup, L.H. Daly and S.H. Wiberley, Introduction to Infrared and Raman Spectroscopy, New York and London, Academic Press, p. 511 (1964).
12. D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli, Infrared and Raman Characteristic Frequencies of Organic Molecules, London, Academic Press, pp. 9-28 (1991).
13. R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, New York, John Wiley, p. 104 (1991).
14. A.I. Balabanovich, A. Hornunga, D. Merza and H. Seiferta, *Polym. Degrad. Stab.*, **85**, 713 (2004).
15. A. Tiselius, *J. Physical Chem.*, **40**, 223 (1936).
16. H. Pfeifer, W. Schirmer and H. Winkler, *Advan. Chem. Ser.*, **121**, 430 (1973).