

Analyses of Polyethylene Glycol (Mono- and Di- Methyl) Ether Adsorbed on CaA, NaX, NaY, and ZSM-5 Synthetic Zeolites by Infrared and Raman Spectroscopies

Nuri ÖZTÜRK^{1*}, Semiha BAHÇELİ²

Abstract

The adsorptions of polyethylene glycol monomethyl ether (PEGMME) and polyethylene glycol dimethyl ether (PEGDME) on CaA, NaX, NaY, and ZSM-5 zeolites have been analyzed by using experimental FT-IR and Raman spectroscopies. The vibration wavenumbers of polymers adsorbed on zeolites have been reported and the adsorption properties of zeolites with different molecular sizes and cations have been compared. Disappearing of some vibration modes of polymers or shifts to the higher and lower frequency region after the polymers have been adsorbed on zeolites; indicates an interaction between polymers and zeolites. By considering the obtained experimental spectral results we can suggest that the source of adsorption of polymers on zeolites can be based on the interactions between OH groups or oxygen atoms settled in polymer chains and the silanol hydroxyl groups on the surface of each zeolite.

Keywords: Vibrational spectroscopy, Zeolite, Adsorption, Polymer.

CaA, NaX, NaY ve ZSM-5 Sentetik Zeolitleri Üzerine Adsorbe Edilen Polietilen Glikol (Mono- ve Di- Metil) Eterin Kırmızıaltı ve Raman Spektroskopileri ile Analizi

Öz

Polietilen glikol monometil eter (PEGMME) ve polietilen glikol dimetil eterin (PEGDME) CaA, NaX, NaY ve ZSM-5 zeolitleri üzerindeki adsorpsiyonları deneysel FT-IR ve Raman spektroskopileri kullanılarak analiz edilmiştir. Zeolitler üzerine adsorbe edilen polimerlerin titreşim dalgasayıları bildirilmiş ve farklı moleküler boyutlara ve katyonlara sahip zeolitlerin adsorpsiyon özellikleri karşılaştırılmıştır. Polimerlerin bazı titreşim modlarının kaybolması veya polimerler zeolitler üzerine adsorbe edildikten sonra daha yüksek ve daha düşük frekans bölgesine kaymalar; polimerler ve zeolitler arasındaki etkileşimin varlığını göstermektedir. Elde edilen deneysel spektral sonuçları dikkate alarak, polimerlerin zeolitler üzerindeki adsorpsiyon kaynağının, OH grupları veya polimer zincirlerine yerleşmiş oksijen atomları ile her bir zeolit yüzeyindeki silanol hidroksil grupları arasındaki etkileşimlere dayandırılabilceğini söyleyebiliriz.

Anahtar Kelimeler: Titreşim spektroskopisi, Zeolit, Adsorpsiyon, Polimer.

¹Giresun University, Dereli Vocational School, Giresun, Türkiye, nuri.ozturk@giresun.edu.tr

²University of Turkish Aeronautical Association, Department of Astronautical Engineering, Ankara, Türkiye, s.bahceli80@gmail.com

¹<https://orcid.org/0000-0001-8742-0160> ²<https://orcid.org/0000-0002-5614-325X>

1. Introduction

The zeolites are crystalline aluminosilicates that exhibit three-dimensional structures interconnecting frameworks of SiO_4 and AlO_4 tetrahedra, being connected by sharing one oxygen atom between two tetrahedra. Low SiO_2 ratio normally provides stronger adsorbance for polar molecules and powerful cation exchange capacity. Conversely, a higher SiO_2 ratio generally provides stronger-acid catalytic activity as adsorbents (Cejka, 2007). Zeolites with low and medium Si/Al ratios can be used to remove water from organic materials, while molecular sieves with a high Si/Al ratio can be used to remove organic materials from water. In other words, zeolites are separated from each other by structural differences in their unit cell and the structural properties of zeolites are highly described in the literature. Zeolites are used as ion exchangers because their cations are bound by weak bonds and ions can be easily exchanged. Zeolites which are used as selective catalysts, ion exchangers, and adsorbents in the oil refinery, petrochemical, and chemical process industries, are the best known microporous molecular sieves. When zeolites are heated, the water molecules in their pores easily leave the zeolitic structure. Depending on the pore structures of the zeolites, it is known that they can adsorb molecules smaller than their pore sizes into the spaces inside them and they can adsorb the molecules with large sizes on their surfaces. The unit cells of the synthetic zeolites CaA, NaX, NaY, and ZSM-5 used in this study consist of $\text{Ca}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}].27\text{H}_2\text{O}$, $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}].264\text{H}_2\text{O}$, $\text{Na}_{56}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{136}].250\text{H}_2\text{O}$ and $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}.16\text{H}_2\text{O}$, respectively (Öztürk et al., 2005; Thomas and Klinowski, 2007; Öztürk et al., 2010). The pore sizes of the mentioned zeolites are 4-5 Å for CaA, 7-10 Å for NaX and NaY, and 5-6 Å for ZSM-5 which consists of two types of crossing and vertical channel systems (Öztürk et al., 2009; Bleken et al., 2011). Most of the newly synthesized synthetic zeolites have larger pore sizes and higher capacity than most natural zeolites, thus allowing applications for larger molecules (Sherman, 1999; Cundy and Cox, 2003; Franus et al., 2014). The catalytic properties of these molecular sieves, which we can think as strong catalysts and sorbents, can be understood by examining the adsorption qualities on their surfaces (Hunger, 1997; Çiçet et al., 2003). Vibration spectroscopy is one of the frequently used methods to determine some properties of zeolites such as absorbent (Şen et al., 2008; Öztürk et al., 2009; Marković et al., 2017; Kumar et al., 2020; Velvarská et al., 2020). Öztürk et al. have investigated the Infrared and SEM analyses of Polyethyleneglycol-400 adsorbed on zeolites NaA, CaA, NaX and NaY zeolites (Öztürk et al., 2009). It seems that our study is in harmony with this study.

This study aims to notice the results of infrared and Raman spectra of two polymers adsorbed on CaA (LTA, type 5A), NaX (FAU, type 13X), NaY (FAU), and ZSM-5 (MFI) synthetic zeolites and the source of adsorption of polyethylene glycol (monomethyl ether) and polyethylene glycol

(dimethyl ether) on mentioned zeolites. It is seen that the adsorption sources of polymers on zeolites are the interactions between methylene and OH groups and oxygen atoms of the polymers and the non-acidic silanol hydroxyl group on the surface of zeolites.

2. Materials and Methods

2.1. Materials

All synthetic zeolites, CaA (Aldrich), NaX (Fluka), NaY (Aldrich), and ZSM-5 (Zeolisynt, Si/Al ratio: 30) have been obtained from commercial sources. Moreover, PEGMME (Fluka) powder and liquid PEGDME (Fluka) have been obtained commercially and used without any purification. Chloroform and ethyl alcohol are used as solvent and purifier to remove residues.

2.2. Sample Preparation

First, CaA, NaX, and NaY zeolites have been calcined (activated in the oven) at 623K for 4 hours, while, ZSM-5 has been activated at 823K for 5 hours to be purified from water molecules in their structure and waited for them to cool to room temperature. 100 mg PEGMME powder has been solved in 40 ml chloroform without concentration calculation. Then, 1 g of each zeolite has been put into 10 ml PEGMME solution and liquid PEGDME separately. After the samples have been stirred and stored for 40 hours for maximum adsorption to occur at room temperature, the mixtures have been filtered and washed three times with chloroform and ethyl alcohol to remove suspension residues. All samples have been left to dry at room temperature.

2.3. Measurements

The polymer adsorbed zeolite samples have been compressed as pellets with KBr for the infrared spectrum. The IR spectra of the samples have been recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer in the transmission mode in the region of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} at room temperature. Raman spectra of the samples have been recorded by using a Jasco NRS-3100 micro-Raman Spectrophotometer with 600 lines/mm grating in the region of 4000–150 cm^{-1} at room temperature. The 785 nm lines of the diode laser have been used for the excitation of samples. The exposure time for each sample has been taken as 25 seconds and the average of 10 measurements taken. Infrared and Raman spectra of PEGMME and PEGDME have been also taken by the mentioned methods.

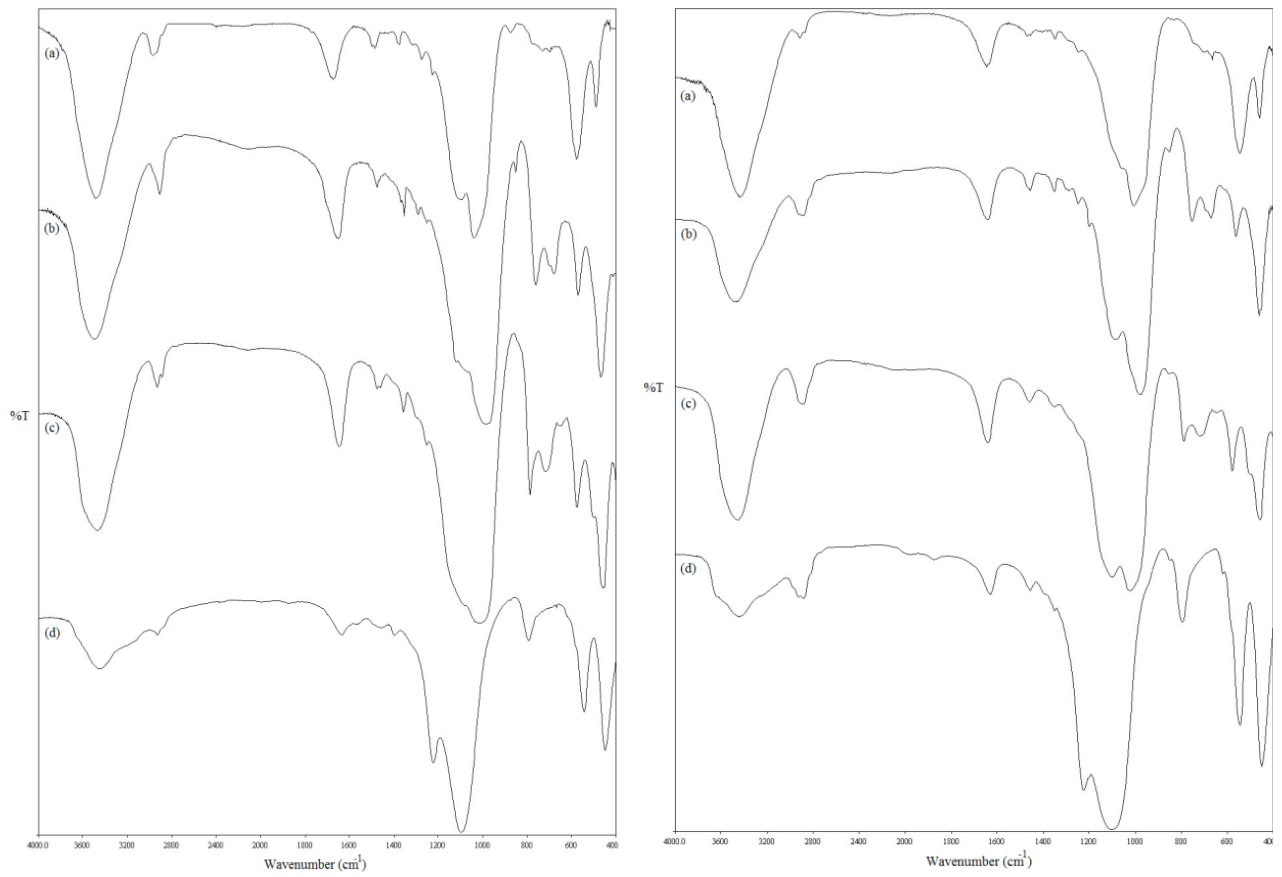


Figure 2. Infrared spectra of PEGMME (left) and PEGDME (right) adsorbed on the a) CaA, b) NaX, c) NaY and d) ZSM-5 zeolites

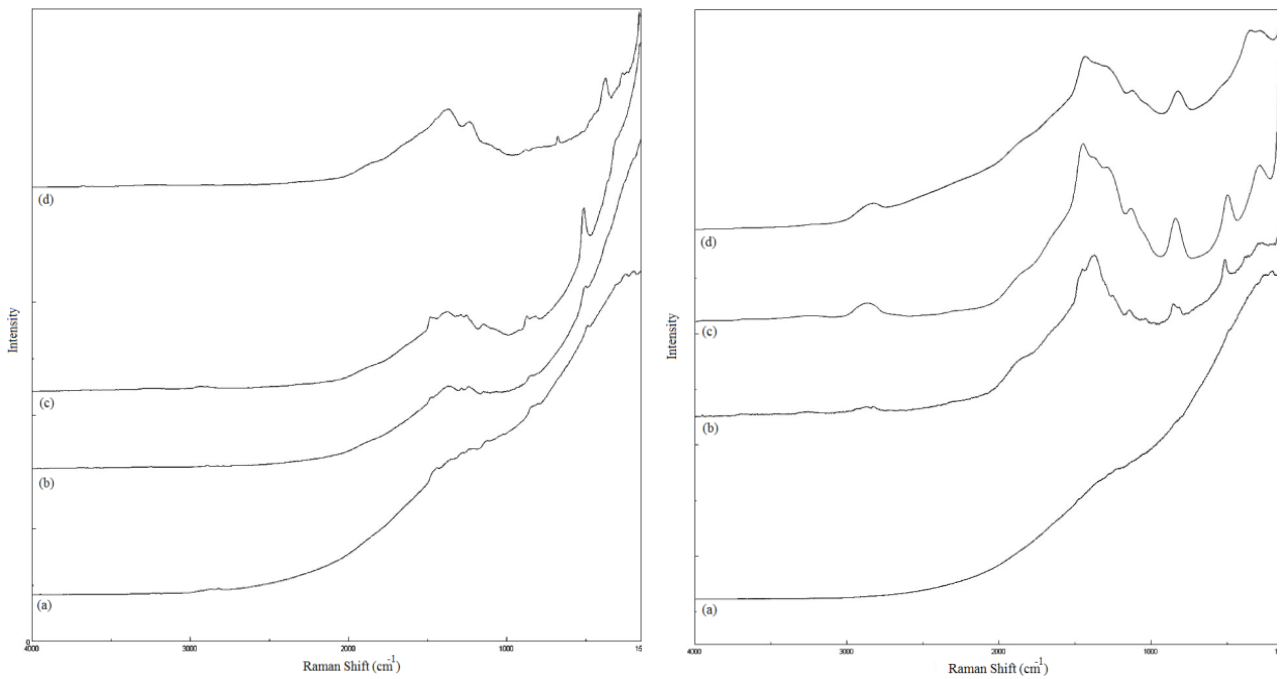


Figure 3. μ -Raman spectra of PEGMME (left) and PEGDME (right) adsorbed on the a) CaA, b) NaX, c) NaY and d) ZSM-5 zeolites

Table 1. The IR and Raman frequencies (cm⁻¹) of PEGMME adsorbed on CaA, NaX, NaY, and ZSM-5 zeolites.

PEGMME		CaA		NaX		NaY		ZSM-5		Assignments
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
2947 w	2943 w	2926 m	-	2949 sh	-	2928 m	2936 vw	2928 m	2932 vw	$\nu_{as}(\text{CH}_3)$
2881 s	2886 m	2881 sh	2870 vw	2892 m	2885 vw	2887 w	2892 vw	2874 sh	2881 vw	$\nu_{as}(\text{CH}_2)$
2861 vw	2830 w	2835 sh	2820 vw	2806 sh	-	-	-	-	-	$\nu_s(\text{CH}_2)$
1467 s	1481 s	1473 m	-	1468 m	1475 w	1477 m	1477 m	-	-	$\delta_s(\text{CH}_2)$
1456 w	1447 w	1458 m	1442 w	1457 w	-	1460 m	1450 vw	1456 bm	1448 vw	$\delta(\text{CH}_3)$
1360 m	1362 w	1357 sh	-	1360 w	-	1357 m	-	-	1371 bm	$w(\text{CH}_2)$
1341 s	-	1350 m	-	1344 m	-	-	-	1323 sh	-	$w(\text{CH}_2)$
1279 s	1280 s	1294 bw	1277 w	1282 m	1285 w	1300 w	1282 w	-	-	$t(\text{CH}_2)$
1241 s	1234 m	1250 m	-	1243 m	-	1252 w	-	-	1230 bm	$t(\text{CH}_2)$
1147 s	1141 m	-	-	1111 w	-	-	-	-	-	$w(\text{CH}_3)$
-	1129 sh	-	1123 w	-	1144 w	-	-	-	1124 w	$\rho(\text{CH}_2)$
1060 s	1063 m	1071 bm	-	1063 w	1067 vw	1083 bw	-	-	1046 w	$\nu(\text{C-O})$
947 m	934 w	-	-	-	-	-	921 w	-	-	$\nu(\text{C-O-C})$
841 s	844 s	850 m	838 w	843 m	839 w	844 sh	862 m	-	872 w	$\rho(\text{CH}_2)$
-	803 vw	-	803 w	-	812 vw	-	807 w	-	-	$w(\text{CH}_2)$

v: very; s: strong; m: medium; w: weak; sh: shoulder; b: broad; ν : stretching; δ : in-plane bending; δ_s : scissoring; w: wagging; t: twisting; ρ : rocking

Besides, there are some significant changes for the CH₂ in-plane bending, scissoring, wagging, twisting, and rocking bands among free and adsorbed polymers as seen in Tables 1 and 2. The shifts to higher or lower frequency regions in the IR and μ -Raman spectra of polymers adsorbed on the mentioned zeolites indicate that the silanol hydroxyl groups on the surface of zeolites interact with methylene groups of adsorbed polymers by hydrogen bonding (Silverstein and Webster, 1997; Stuart, 2004).

Table 2. The IR and Raman frequencies (cm⁻¹) of PEGDME adsorbed on CaA, NaX, NaY, and ZSM-5 zeolites.

PEGDME		CaA		NaX		NaY		ZSM-5		Assignments
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
2924 sh	2937 sh	2932 sh	-	2928 sh	-	-	-	2929 m	-	$\nu_{as}(\text{CH}_3)$
2872 vs	2872 s	2883 m	-	2882 m	2880 w	2889 m	2878 bm	2879 m	-	$\nu_s(\text{CH}_2)$
2823 sh	2823 s	2831 sh	-	2830 sh	2828 w	2824 sh	-	2826 sh	2841 bm	$\nu_s(\text{CH}_2)$
1470 sh	1471 vs	1471 sh	1479 w	1471 sh	-	1462 m	-	-	-	$\delta_s(\text{CH}_2)$
1455 vs	1451 vs	1457 m	-	1456 m	1444 w	-	1452 s	1457 m	1445 bm	$\delta(\text{CH}_3)$
1350 vs	1369 m	1353 m	-	1351 m	-	1355 m	-	1351 w	1366 w	$w(\text{CH}_2)$
1299 s	1286 s	1287 m	1279 w	1286 m	1296 sh	1288 w	1292 bm	-	1296 w	$w(\text{CH}_2)$
1247 s	1244 m	1249 m	-	1250 m	-	1249 m	-	-	-	$t(\text{CH}_2)$
1199 vs	1208 sh	1199 m	-	1200 m	-	1197 sh	-	1202 w	-	$\delta(\text{CH}_3)$
1105 vs	1135 s	1102 m	-	1102 m	1138 m	1106 m	-	-	1130 m	$\nu(\text{C-O})$
1028 m	1030 m	-	-	1022 sh	-	1026 m	1040 sh	-	1037 w	$\nu_s(\text{C-C})$
943 s	930 m	-	-	-	-	-	-	951 sh	-	$\nu_s(\text{C-O-C})$
851 vs	849 vs	849 m	842 vw	850 m	850 m	849 m	841 m	850 w	834 bm	$\rho(\text{CH}_2)$
-	811 sh	-	805 vw	-	812 w	-	-	-	-	$\rho(\text{CH}_2)$
-	284 bm	-	-	-	282 bm	-	-	-	296 bm	$\delta(\text{C-O-C})$

v: very; s: strong; m: medium; w: weak; sh: shoulder; b: broad; ν : stretching; δ : in-plane bending; δ_s : scissoring; w: wagging; t: twisting; ρ : rocking

However, the strong and medium C-O stretching band of free PEGMME at 1060 (IR) cm^{-1} – 1063 (R) cm^{-1} have been observed at 1071 cm^{-1} , 1063 cm^{-1} and 1083 cm^{-1} for IR spectra of PEGMME adsorbed on CaA, NaX, and NaY, respectively, and at 1067 cm^{-1} and 1046 cm^{-1} for Raman spectra of polymer adsorbed on NaX and ZSM-5, respectively. Similarly, the medium C-O-C stretching band of free PEGMME (Silverstein and Webster, 1997; Stuart, 2004; Abdel-Mohsen et al., 2012) at 947 (IR) cm^{-1} – 934 (R) cm^{-1} has been only observed at 1021 cm^{-1} for the Raman spectrum of polymer adsorbed on NaY as a weak band and not observed for IR spectra. While most of the characteristic bands of PEGMME have been also observed in their adsorbed form on zeolites, the bending and stretching modes of the OH band have been not observed in any of the IR and Raman spectra.

On the other hand, the very strong C-O stretching band of free PEGMME at 1105 cm^{-1} for IR spectrum and strong for Raman spectrum at 1135 cm^{-1} have been observed as a medium band at 1102 cm^{-1} , 1102 cm^{-1} and 1106 cm^{-1} for IR spectra of PEGDME adsorbed on CaA, NaX, and NaY, respectively, and at 1138 cm^{-1} and 1130 cm^{-1} for Raman spectra of PEGMME adsorbed on NaX and ZSM-5, respectively. Moreover, the C-O-C stretching band of PEGDME at 943 cm^{-1} has been observed as a shoulder at 951 cm^{-1} in the IR spectrum of ZSM-5. This band has not been observed in the Raman spectrum of any zeolite that adsorbed the PEGDME. Besides, C-O-C bending mode has been observed at 284 cm^{-1} , 282 cm^{-1} and 296 cm^{-1} as a broad medium band in the Raman spectra of pure PEGDME, the adsorbed form of NaX and ZSM-5, respectively. The shifts at the positions of most of the characteristic vibrational bands of polymer adsorbed on zeolites show the interaction between zeolites and polymers.

4. Conclusions

The peaks that did not exist before in the infrared spectra of zeolites but appear in the spectra after the polymers were adsorbed belong to the polymers. These peaks of polymers show that the adsorption process has taken place. The experimental IR and μ -Raman spectral results of polyethylene glycol (monomethyl ether) and polyethylene glycol (dimethyl ether) adsorbed on the CaA, NaX, NaY, and ZSM-5 synthetic zeolites indicate that the sources of adsorptions of polymers on title zeolites seem to be the interactions between the methylene and OH groups of polymers and oxygen atoms located in polymer chains and the non-acidic silanol hydroxyl group on the surface of the zeolites employing a hydrogen bond.

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Authors' Contributions

All authors contributed equally to the study

Statement of Conflicts of Interest

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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