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

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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.
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 Ca$_{12}$(AlO$_2$)$_2$(SiO$_2$)$_2$.27H$_2$O, Na$_{86}$(AlO$_2$)$_{86}$(SiO$_2$)$_{106}$.264H$_2$O, Na$_{56}$(AlO$_2$)$_{86}$(SiO$_2$)$_{136}$.250H$_2$O and Na$_n$Al$_n$Si$_{96-n}$O$_{192-1.6}$H$_2$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 (Zeolisyt, 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.
3. Results and Discussion

The molecular structures of polymers have been depicted in Figure 1. Infrared (IR) spectra of polyethylene glycol (monomethyl ether) and polyethylene glycol (dimethyl ether) adsorbed on CaA, NaX, NaY, and ZSM-5 have been given in Figure 2. Similarly, the Raman (R) spectra of polyethylene glycol (monomethyl ether) and polyethylene glycol (dimethyl ether) adsorbed on the mentioned zeolites have been given in Figure 3. On the other hand, the observed wavenumbers and the assignments of vibrational bands have been summarized in Table 1 and Table 2 as well as those of free PEGMME and PEGDME, respectively. According to the tables, we can say that the most characteristic vibration bands of both polymers have been also observed for their adsorbed forms on the mentioned zeolites. As can be seen in Figures 2 and 3, some characteristic peaks of both polymers were generally observed as weak bands in the IR and Raman spectra of zeolites after the adsorption process. When the IR and Raman spectra of pure zeolites are compared with the spectra recorded after the adsorption process on zeolites, the observed extra bands are caused by the adsorbed polymers. The loss of vibration modes of pure polymers or changes in the position of any vibration mode would be a sign of interaction between polymers and synthetic zeolites. In comparison with vibrational bands of free polymers, the shifts at the positions of vibration bands of polymers adsorbed on mentioned zeolites can be concluded to be an interaction between zeolites and polymers. These frequency shifts to lower and higher regions show the presence of adsorption of PEGMME and PEGDME on the mentioned zeolites. Then, the adsorption properties of zeolites with different molecular sizes have been compared. As seen in Table 1, the CH$_2$ and CH$_3$ stretching bands at the interval of 2947-2861 (IR) cm$^{-1}$ and 2943-2830 (R) cm$^{-1}$ of free PEGMME have been observed at the interval of 2949-2806 (IR) cm$^{-1}$ and 2936-2820 (R) cm$^{-1}$ of adsorbed forms on zeolites. Similarly, as seen in Table 2, these bands have observed at the interval of 2924-2823 (IR) cm$^{-1}$ and 2937-2823 (R) cm$^{-1}$ for free PEGDME and at the interval of 2932-2824 (IR) cm$^{-1}$ and 2880-2828 (R) cm$^{-1}$ for adsorbed forms on mentioned zeolites. Likewise; Öztürk et al. observed CH$_2$ symmetric and asymmetric stretching vibrations in the range of 2918-2745 cm$^{-1}$ in their studies (Öztürk, et al., 2009). Some other vibration band assignments in Table 1 and Table 2 are also in agreement with this study. Moreover, very weak bands of around 2900-3000 cm$^{-1}$ can be assigned to the presence of SiOCH$_3$, called a chemisorption product, on zeolites (Çiçek et al., 203).

![Figure 1. Molecule structures of a) PEGMME and b) PEGDME](image-url)
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 | IR | Raman | Assignments |
| 2947 w | 2943 w | 2926 m | - | 2949 sh | - | 2928 m | 2936 vw | 2928 m | 2932 vw | vₐ(CH₃) |
| 2881 s | 2886 m | 2881 sh | 2870 vw | 2892 m | 2885 vw | 2887 w | 2892 vw | 2874 sh | 2881 vw | vₐ(CH₃) |
| 2861 vw | 2830 w | 2835 sh | 2820 vw | 2806 sh | - | - | - | - | - | ρ(CH₂) |
| 1467 s | 1481 s | 1473 m | - | 1468 m | 1475 w | 1477 m | 1477 m | - | - | δ(CH₂) |
| 1456 w | 1447 w | 1458 m | 1442 w | 1457 w | - | 1460 m | 1450 vw | 1456 bm | 1448 vw | δ(CH₂) |
| 1360 m | 1362 w | 1357 sh | - | 1360 w | - | 1357 m | - | - | 1371 bm | w(CH₃) |
| 1341 s | - | 1350 m | - | 1344 m | - | - | - | 1323 sh | - | w(CH₃) |
| 1279 s | 1280 s | 1294 bw | 1277 w | 1282 m | 1285 w | 1300 w | 1282 w | - | - | t(CH₂) |
| 1241 s | 1234 m | 1250 m | - | 1243 m | - | 1252 w | - | - | 1230 bm | t(CH₂) |
| 1147 s | 1141 m | - | - | 1111 w | - | - | - | - | - | w(CH₂) |

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 | IR | Raman | Assignments |
| 2924 sh | 2937 sh | 2932 sh | - | 2928 sh | - | - | - | 2929 m | - | vₐ(CH₃) |
| 2872 vs | 2872 s | 2883 m | - | 2882 m | 2880 w | 2889 m | 2878 bm | 2879 m | - | ρ(CH₂) |
| 2823 sh | 2823 s | 2831 sh | - | 2830 sh | 2828 w | 2824 sh | - | 2826 sh | 2841 bm | ρ(CH₂) |
| 1470 sh | 1471 vs | 1471 sh | 1479 w | 1471 sh | - | 1462 m | - | - | - | δ(CH₂) |
| 1455 vs | 1451 vs | 1457 m | - | 1456 m | 1444 w | - | 1452 s | 1457 m | 1445 bm | δ(CH₂) |
| 1350 vs | 1369 m | 1353 m | - | 1351 m | - | 1355 m | - | 1351 w | 1366 w | w(CH₂) |
| 1299 s | 1286 s | 1287 m | 1279 w | 1286 m | 1296 sh | 1288 w | 1292 bm | - | 1296 w | w(CH₂) |
| 1247 s | 1244 m | 1249 m | - | 1250 m | - | 1249 m | - | - | - | t(CH₂) |
| 1199 vs | 1208 sh | 1199 m | - | 1200 m | - | 1197 sh | - | 1202 w | - | δ(CH₂) |
| 1105 vs | 1135 s | 1102 m | - | 1102 m | 1138 m | 1106 m | - | - | 1130 m | ν(C-O) |
| 1028 m | 1030 m | - | - | 1022 sh | - | 1026 m | 1040 sh | - | 1037 w | ρ(CH₂) |
| 943 s | 930 m | - | - | - | - | - | 951 sh | - | - | ν(C-O-C) |
| 851 vs | 849 vs | 849 m | 842 vw | 850 m | 850 m | 849 m | 841 m | 850 w | 834 bm | ρ(CH₂) |
| - | 811 sh | 805 vw | - | 812 w | - | - | - | - | - | ρ(CH₂) |
| - | 284 bm | - | - | 282 bm | - | - | - | - | - | ρ(CH₂) |

v: very; s: strong; m: medium; w: weak; sh: shoulder; b: broad; v: stretching; δ: in-plane bending; 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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