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Research Article

Infrared and Raman Spectroscopic Analyses of Poly(allylamine) Adsorbed on CaA, NaX, NaY, and ZSM-5 Synthetic Zeolites

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Abstract

The adsorptions of poly(allylamine) solution on CaA, NaX, NaY, and ZSM-5 zeolites have been investigated by using FT-IR and micro-Raman spectroscopies. Vibrational wavenumbers of poly(allylamine) adsorbed on the mentioned zeolites have been reported and the adsorption characteristics of zeolites with different cations and molecular sizes have been compared. The small shifts to the high or low-frequency regions in the position of vibration modes or the disappearance of the vibration bands show that there are interactions between poly(allylamine) and zeolites. By considering the obtained results, we can say that the adsorption source of polymer on the mentioned zeolites can withstand the interaction between the amine group of polymer and the silanol hydroxyl group on the surface of the zeolites.

Keywords: IR and Raman spectroscopies, Zeolite, Poly(allylamine), Adsorption

CaA, NaX, NaY ve ZSM-5 Sentetik Zeolitleri Üzerine Adsorbe Edilen Poli(allilamin)'in Kırmızıaltı ve Raman Spektroskopileri ile Analizi

Öz

Poli(allilamin) çözeltisinin CaA, NaX, NaY ve ZSM-5 zeolitleri üzerindeki adsorpsiyonları FT-IR ve mikro-Raman spektroskopileri kullanılarak araştırılmıştır. Bahsedilen zeolitler üzerine adsorbe edilmiş poli(allilamin) titreşim dalgasayıları rapor edilmiş ve farklı katyonlara ve moleküler boyutlara sahip zeolitlerin adsorpsiyon özellikleri karşılaştırılmıştır. Titreşim modlarının konumundaki düşük veya yüksek frekans bölgelerine kaymalar ya da titreşim bantlarının kaybolması, poli(allilamin) ve zeolitler arasında etkileşimler olduğu anlamına gelir. Elde edilen sonuçları dikkate alarak, bahsedilen zeolitler üzerindeki polimerin adsorpsiyon kaynağının, polimerin amin grubu ile zeolitlerin yüzeyi üzerindeki silanol hidroksil grubu arasındaki etkileşime dayanabileceğini söyleyebiliriz.

Anahtar Kelimeler: IR ve Raman spektroskopileri, Zeolit, Poli(allilamine), Adsorpsiyon

1. Introduction

Zeolites with microsizes of their pores signify a very important group of porous materials with respect to their applications as adsorbents, ion-exchangers or mainly heterogeneous catalysts. The zeolites, which are the best-known microporous molecular sieves, are crystalline aluminosilicates having a framework-type structure including AlO_4 and SiO_4 tetrahedra bonded by sharing an oxygen atom between two tetrahedral (Weitkamp and Puppe, 1999). It is known that zeolites adsorb the molecules, which have a particular size on their pore structures. As the pores preferably adsorb the molecules

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that suitable easily inside the pores and keep out the molecules larger than the pore size of the zeolite, they act as sieves for molecules. We can consider the zeolites as powerful sorbents and catalysts. The catalytic properties of these molecular sieves can be understood by examining the adsorption characteristics of the reactions on the surface of the zeolites. (Bahçeli and Gökce, 2015; Çiçek et al., 2003; Hunger; 1997; Klinowski, 1993).

On the other hand, in many sciences, such as biology, medicine, and petrology, there is a great interest in water-soluble polymers, and many scientific studies are being conducted on their biological and chemical properties. In particular, they are commonly used as plasma substituents and in controlled drug release (Rivas and Pereira, 2000a and b; Sarkar and Kershner, 1996). Poly(allylamine) (in short PAA) is one of the water-soluble cationic polymers has an amino group as a ligand group with primary amino groups and has a chemical formula as $H(C_3H_5N)_nH$. At the same time, PAA is an interesting polymer that is often used in the thin film and metal complexes studies (Fery et al., 2001; Lvov et al., 1993; Rivas and Seguel, 1996). Since water-soluble polymers exhibit pseudoplastic property, the viscosimetric behavior of metal complexes of PAA was investigated by Rivas and Pereira (Rivas and Pereira, 2000a and b). Also, Sung et al. (1997) used poly(allylamine) as a cationic polyelectrolyte solute.

The purpose of this study is to report the results of infrared and μ-Raman spectra of poly(allylamine) solution adsorbed on zeolites with different cations and pore sizes (CaA (LTA), NaX (FAU), NaY (FAU), and ZSM-5 (MFI)) and the source of adsorption of the poly(allylamine) on zeolites.

2. Experimental Details

All synthetic zeolites used in the study, CaA (Aldrich), NaX (Fluka), NaY (Aldrich) and ZSM-5 (Zeolisyt, Si/Al ratio: 30), were obtained commercially. The unit cells of CaA, NaX, NaY and ZSM-5 consist of $Ca_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$, $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].264H_2O$, $Na_{56}[(AlO_2)_{86}(SiO_2)_{136}].250H_2O$ and $Na_nAl_nSi_{96-n}O_{192}.16H_2O$, respectively (Öztürk et al., 2005; Öztürk and Bahçeli, 2006; Thomas and Klinowski, 2007). The pore sizes of 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 intersecting and perpendicular channel systems (Öztürk et al., 2005; Viswanadham et al., 1997). Furthermore, the PAA solution (Aldrich, 20 wt. % solution in water) was obtained commercially and used without any purification. The schematic representation of the PAA was given in Figure 1.

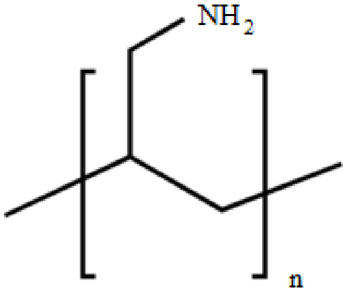

Figure 1. The schematic representation of poly(allylamine).

First, CaA, NaX and NaY zeolites were calcinated to activate for 4 hours at 623 K and ZSM-5 was activated for 5 hours at 823 K. Then, 1 g of each of the zeolites was placed into 10 cm^3 of the PAA solution in a beaker. After the mixtures were stirred for

40 h, filtered and washed three times with ethanol to remove suspension residues. Finally, ethanol was completely evaporated at room temperature.

The IR spectra of samples were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer in transmission mode with a resolution of 4 cm^{-1} at room temperature. The samples were compressed as pellets and placed into an equipped with KBr window. The Raman spectra of the samples were collected by using a Jasco NRS-3100 micro-Raman spectrometer (600 lines/mm grating) in the region of 100-4000 cm^{-1} at room temperature. The 785 nm lines of the diode laser was used for excitation with objective 100x. The average of 10 scans was obtained and the exposure time was set to 25 seconds for each measurement.

3. Results and Discussion

The IR spectra of PAA adsorbed on CaA, NaX, NaY, and ZSM-5 zeolites were given for two frequency ranges in Figure 2 (3400-2800 cm^{-1}) and Figure 3 (1700-650 cm^{-1}).

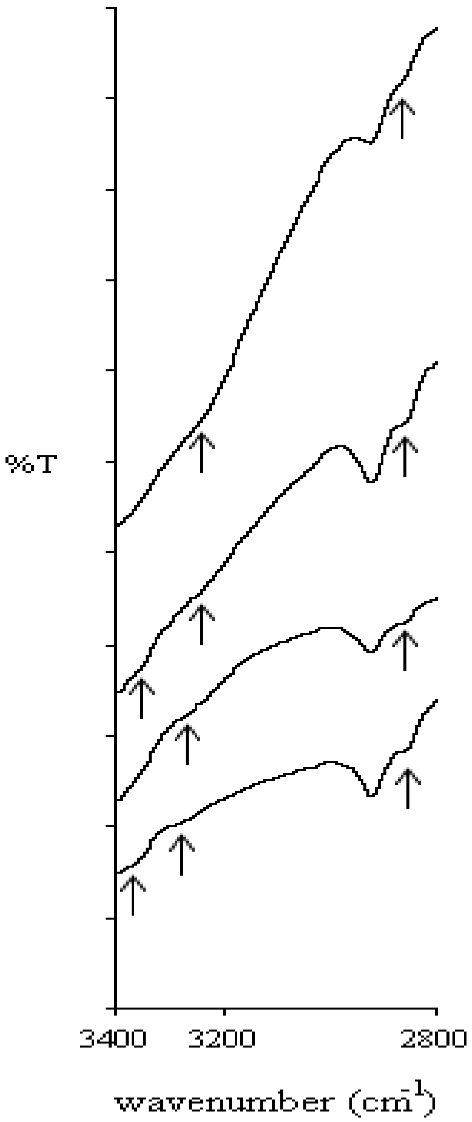

Figure 2. Infrared spectra of poly(allylamine) adsorbed on the CaA, NaX, NaY and ZSM-5 zeolites (from top to bottom) at the interval of 3400-2800 cm^{-1}.

Similarly, The μ-Raman spectra of PAA adsorbed on the mentioned synthetic zeolites were given for two frequency ranges in Figure 4 (3400-2800 cm^{-1}) and Figure 5 (1700-650 cm^{-1}).

On the other hand, the observed wavenumbers and the assignments of the IR and Raman vibrational bands were summarized in Table 1 as well as those of free PAA.

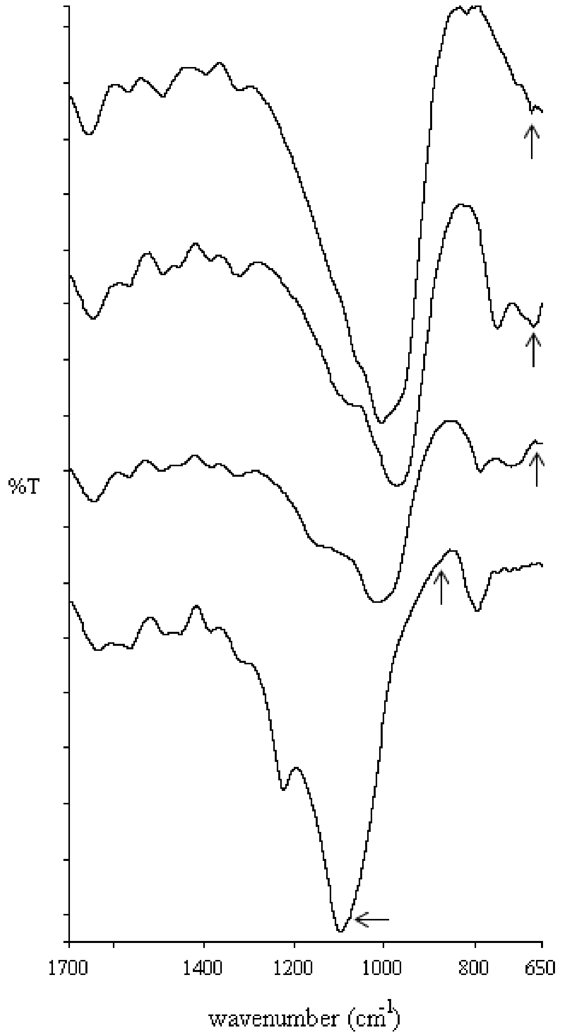

Figure 3. Infrared spectra of poly(allylamine) adsorbed on the CaA, NaX, NaY and ZSM-5 zeolites (from top to bottom) at the interval of 1700-650 cm^{-1}.

As shown in Table 1, the characteristic vibration bands of the PAA were also observed in the adsorbed form on the zeolites. The shift to the low or high-frequency region in the position of any vibration mode or the disappearance of the vibration band means that there is an interaction between PAA and zeolites.

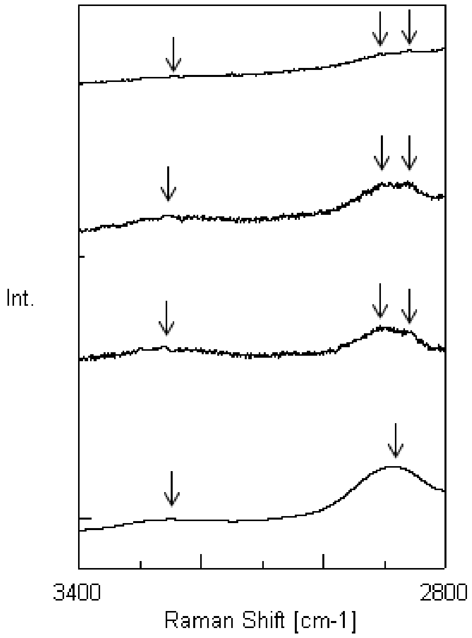

Figure 4. μ-Raman spectra of poly(allylamine) adsorbed on the CaA, NaX, NaY and ZSM-5 zeolites (from top to bottom) at the interval of 3400-2800 cm^{-1}.

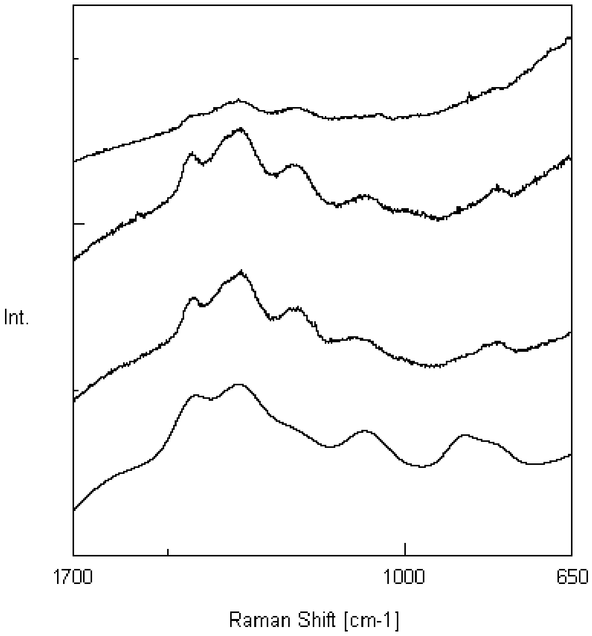

Figure 5. μ-Raman spectra of poly(allylamine) adsorbed on the CaA, NaX, NaY and ZSM-5 zeolites (from top to bottom) at the interval of 1700-650 cm^{-1}.

For example, the observed band at 3355 (IR) cm^{-1} in the higher frequency region was assigned to NH_2 asymmetric stretching vibration of pure PAA and this band was observed at 3352 (IR) and 3370 (IR) cm^{-1} (specified with arrows in Fig. 2) for PAA adsorbed on NaX and ZSM-5, respectively. Likewise, the NH_2 asymmetric stretching band at 3284 (IR) - 3298 (R) cm^{-1} of free PAA were observed at the interval of 3279-3292 (IR) and 3247-3267 (R) cm^{-1} (specified with arrows in Figure 2 and 4) in the IR and Raman spectra of PAA adsorbed on CaA, NaX, NaY, and ZSM-5 which were shifted slightly to the lower or higher frequency region (Silverstein, 2005). On the other hand, the NH_2 scissoring band at 1639 (IR) - 1635 (R) cm^{-1} of free PAA was observed at the interval of 1650-1633 cm^{-1} in the IR spectra of PAA adsorbed on NaX, NaY, and ZSM-5, respectively. But, this band was observed only in the Raman spectra of PAA adsorbed on ZSM-5 at 1621 cm^{-1}. Moreover, after the adsorption treatment, the NH_2 wagging band at 890 (IR) - 881 (R) cm^{-1} of pure PAA was localized at 891 (R) cm^{-1} and 875 (IR) - 874 (R) cm^{-1} on NaY and ZSM-5, respectively (Silverstein et al., 2005; Stuart, 2004). Similarly, the NH_2 rocking band at 687 (IR) - 695 (R) cm^{-1} for the mentioned polymer was given rise to absorption bands at 663, 664 and 657 cm^{-1} (specified with arrows in Fig. 3) in IR spectra of CaA, NaX and NaY after the adsorption treatment, respectively. These significant shifts to lower frequency region can be considered to be adsorbed as surface amine ions on zeolites.

The observed bands at 2912 (IR) - 2902 (R) cm^{-1} (asymmetric stretching) and 2851 (IR) - 2864 (R) cm^{-1} (symmetric stretching) that are corresponded to CH_2 stretching vibrational bands of free PAA were occurred at the interval of 2926-2864 (IR) - 2929-2858 (R) cm^{-1} in IR and Raman spectra of PAA adsorbed on title zeolites (shoulders were shown with an arrow in Fig. 2). On the other hand, the deformation modes (scissoring, wagging, rocking and twisting) of the CH_2 group were observed at the interval of 1575-1125 cm^{-1} in the IR spectrum and in the region of 1554-1344 cm^{-1} in the Raman spectrum of the free PAA. For example, the scissoring modes were observed at 1571 (IR) - 1597 (R), 1492 (IR) and 1452 (R) cm^{-1} (for CaA), 1567 (IR) - 1561 (R), 1494 (IR) and 1456 (IR) - 1450 (R) cm^{-1} (for NaX), 1567 (IR) - 1556 (R) and 1456 (IR) - 1448 (R) cm^{-1} (for NaY) and 1565 (IR), 1495 (IR) and 1457 (IR) - 1441 (R) cm^{-1} (for ZSM-5) after absorption procedure. Similarly, the wagging, twisting and rocking modes were given rise to absorption bands in the regions of 1386-1319 cm^{-1} (for CaA), 1335-1104 cm^{-1} (for NaX), 1333-1128 cm^{-1} (for NaY) and 1385-1321 cm^{-1} (for ZSM-5) in IR and Raman spectra of PAA adsorbed on zeolites.

The band at 1083 cm^{-1} in the Raman spectrum of bulk PAA can be assignable to the C-N stretching band of primary aliphatic amines (Taki et al., 1997). Since in this C-N vibration region is possible mixed of several bands, the determination of C-N vibration for aliphatic amine is very difficult. So, this band was observed only in the Raman spectrum of PAA adsorbed on ZSM-5 and shifted to 1087 cm^{-1} (specified with an arrow Fig. 3). Likewise, the observed band in pure PAA at 816 (IR) - 818 (R) cm^{-1} was assigned C-C stretching band which was observed at 820 (IR) - 811 (R) cm^{-1} (for CaA), 805 (R) cm^{-1} (for NaX), 817 (IR) - 806 (R) cm^{-1} (for NaY) and 806 (R) cm^{-1} (for ZSM-5) on absorbed zeolites.

Table 1. Vibrational wavenumbers (cm^{-1}) of poly(allylamine) adsorbed on CaA, NaX, NaY, and ZSM-5 zeolites.

Poly(allylamine)		Poly(allylamine) adsorbed on								Assignment
		CaA		NaX		NaY		ZSM-5		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
3355 m	—	—	—	3352 sh	—	—	—	3370 sh	—	$v_{as}(NH_2)$
3284 m	3298 w	3279 sh	3247 vw	3292 sh	3255 vw	3292 sh	3267 vw	—	3254 vw	$v_s(NH_2)$
2912 s	2902 m	2929 w	2901 vw	2926 m	2903 vw	2925 m	2910 w	2926 m	—	$v_{as}(CH_2)$
2851 m	2864 m	2864 sh	2858 vw	2864 sh	2860 vw	2864 sh	2863 w	2864 sh	2885 bm	$v_s(CH_2)$
1639 sh	1635 w	—	—	1650 m	—	1645 m	—	1633 m	1621 w	$\delta(NH_2)$
1575 s	1554 sh	1571 m	1597 vw	1567 m	1561 vw	1567 m	1556 vw	1565 w	—	$\delta(CH_2)$
1471 sh	—	1492 m	—	1494 sh	—	—	—	1495 w	—	$\delta(CH_2)$
1449 m	1454 s	—	1452 w	1456 w	1450 m	1456 w	1448 m	1457 w	1441 m	$\delta(CH_2)$
1383 m	—	1386 w	—	1385 w	—	1388 w	—	1385 w	—	$w(CH_2)$
1363 sh	1344 s	—	—	1335 m	—	1333 w	—	—	1350 m	$w(CH_2)$
1311 s	—	1319 m	—	1321 m	—	1314 w	—	1321 m	—	$t(CH_2)$
1125 w	—	—	—	1104 sh	—	1128 w	—	—	—	$\rho(CH_2)$
—	1083 m	—	—	—	—	—	—	—	1087 m	v(C-N)
890 bm	881 sh	—	—	—	—	—	891 sh	875 w	874 m	$w(NH_2)$
816 m	818 s	820 w	811 w	—	805 m	817 sh	806 w	—	806 sh	v(C-C)
687 w	695 w	663 w	—	664 w	—	657 vw	—	—	—	$\rho(NH_2)$

v: very; s: strong; m: medium; w: weak; sh: shoulder; b: broad; *v*: stretching; δ: scissoring; *w*: wagging; *t*: twisting; ρ: rocking

4. Conclusions

The frequency shifts observed after adsorption show the presence of the interaction between the zeolites and poly(allylamine). In comparison with vibrational bands of pure polymer, the shifts at the positions of vibration bands of polymer adsorbed on synthetic zeolites can be concluded to be an interaction between zeolite and polymer. Considering the nonacidic silanol hydroxyls at the surfaces and bridging hydroxyl groups at Brönsted acid sites of zeolites as sources of adsorptions, the experimental IR and Raman spectral results of poly(allylamine) adsorbed on the CaA, NaX, NaY, and ZSM-5 synthetic zeolites show that the sources of adsorption of poly(allylamine) on title zeolites appear to interact through a hydrogen bond between the amino group of the polymer and the surface silanol hydroxyl group of synthetic zeolites. As a result, we can say that the poly(allylamine) attacks with the silanol hydroxyls on the surface of synthetic zeolites through the hydrogen bonding where the nitrogen of the amino group acts as a hydrogen bond acceptor.

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