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CaA, NaX ve ZSM-5 Zeolitlerine Adsorbe Edilmiş 2- ve 4-Triflorometilbenzaldehidlerin Kırmızıaltı Spektroskopisi

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Özet: 2- ve 4-triflorometilbenzaldehidlerin (2- ve 4-TFMB) CaA, NaX ve ZSM-5 zeolitlere adsorpsiyonları kırmızıaltı spektroskopisi kullanılarak incelendi. Titreşim frekanslarında gözlenen kaymaların incelendiğinde adsorbe edilmiş 2-TFMB'nin aldehid ve CF_3 gruplarının zeolitlerle etkileşirken 4-TFMB ile zeolitler arasında böyle bir etkileşmenin olmadığını belirledik. Bu etkileşmenin yalnızca molekülün bu iki grubunun birbirlerine yakın oldukları zaman meydana geldiği sonucunu çıkardık.

Anahtar kelimeler: Zeolit, Trifluorometilbenzaldehid, Adsorpsiyon, Kırmızıaltı Spektrumu, Titreşim

Infrared Spectroscopy of 2-and 4-Trifluoromethylbenzaldehydes Adsorbed on Zeolites CaA, NaX and ZSM-5

Abstract: The adsorption of 2- and 4-trifluoromethylbenzaldehydes (2- and 4-TFMB's) on CaA, NaX and ZSM-5 zeolites have been investigated by using FT-IR spectroscopy. On the basis of the observed shifts in the vibrational frequencies we have determined that both the aldehyde and CF_3 groups of the adsorbed 2-TFMB interact with the zeolites while there is no such an interaction between 4-TFMB and the zeolites. We have concluded that such interaction comes out only when these two groups of the molecule are close to each other.

Keywords: Zeolite, Trifluoromethylbenzaldehyde, Adsorption, IR Spectra Vibration

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Introduction

Zeolites are micro porous aluminosilicate, which have diverse properties making them valuable as catalysts, catalyst supports, adsorbents and ion exchange materials in a variety of technological importance process. The catalytic properties of zeolites can be understood by studying the adsorption characteristics of reactant, intermediate and product molecules formed their surface (Coughlan et al. 1981, Mumton 1977). In this area the importance of infrared spectroscopy has been increasingly appreciated during the last decades (Little et al. 1966).

2- and 4-trifluoromethylbenzaldehydes (2- and 4-TFMB's) are benzene derivative molecules, having a chemical formula of [$C_8H_5F_3O$]. In the recent years the coordination chemistry of Schiff bases derived from aldehydes has received much attention (Chen et al. 2006, Sreeletha 2005). Kovacs has investigated the molecular geometries and vibrations of 3- and 4-trifluoromethylphenol by means of quantum chemical calculations and vibrational spectroscopy (Kovacs 2003a, b). In our previous study we have calculated the optimized molecular geometries and complete vibration spectra of 2-, 3- and 4-TFMB's to determine the preferential conformation of the aldehyde (CHO) group in the ground state using ab inito Hartree-Fock, density functional theory and second-order Moller-Plesset methods (Sert et al. 2008).

In this framework we have studied the infrared spectra of 2- and 4-TFMB's adsorbed on the synthetic zeolites CaA, NaX and ZSM-5, and investigated which the groups of TFMB's interact with the zeolites.

Experimental

Synthetic zeolites CaA (type 5A, Aldrich), NaX (type 13X, Fluka) and ZSM-5 (Zeolyst) were obtained from commercial sources. The unit cell of the zeolites CaA, NaX and ZSM-5 (Na form) are $Ca_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$, $Na_{12}[(AlO_2)_{86}(SiO_2)_{106}].264H_2O$ and $Na_nAl_nSi_{96-n}O_{196}.16H_2O$, respectively (Mumton 1977, Scott 1980). The liquid 2- and 4-TFMB's (Aldrich, 98%)] were used without any further purification. Firstly, the zeolites CaA and NaX at 623 K and ZSM-5 at 773 K were activated for 4 and 5 h, respectively. Then, 1g of each zeolite was placed into 10 cm^3 of 2- or 4-TFMB's. After stirring and storing for 40 h the mixtures were filtered and washed twice with ethyl alcohol, and then dried at room temperature.

Samples were compressed into self-supporting pellets and introduced into an IR cell equipped with KBr windows. IR spectra were taken by using a Perkin-Elmer FT-IR (Fourier Transformed Infrared) spectrometer with a resolution of 4 cm^{-1} in the transmission mode.

Results and Discussion

The ab initio optimized structures of 2- and 4 TFMB's are illustrated in Fig. 1 (Sert et al., 2008). They have 17 atoms and 45 normal modes of vibrations. All the vibrations are active both in infrared (IR) and Raman (R). The IR spectra (1650 - 550 cm^{-1}) of 2- and 4-TFMB's adsorbed on the zeolites CaA, NaX and ZSM5 are given in Fig. 2 and Fig. 3, respectively.

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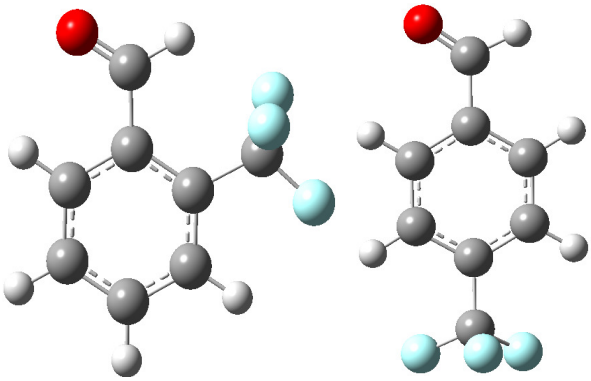

2-TFMB 4-TFMB

Figure 1. *Optimized structures of 2- and 4- TFMB's.*

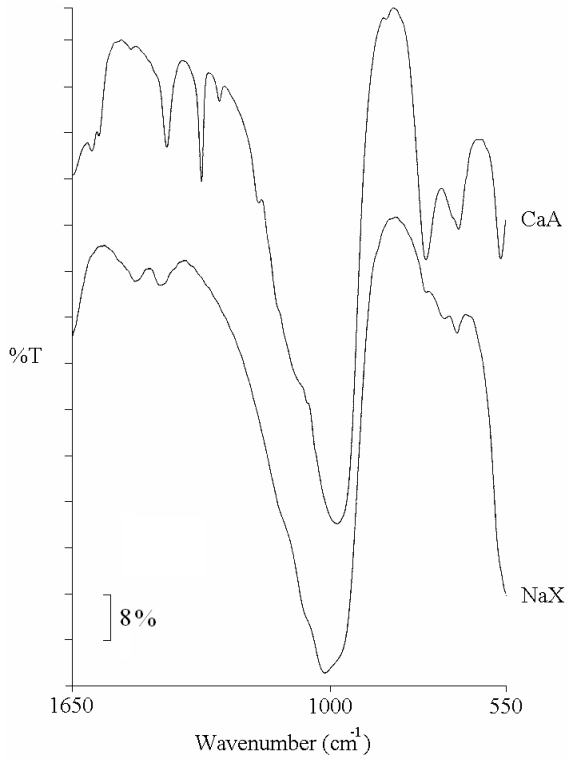

Figure 2. *Infrared spectra of 2-TFMB adsorbed on CaA and NaX zeolites*

The data obtained from the IR spectra are summarized in Table 1 and Table 2. For comparison the tables also include the experimental vibrational frequencies of the bulk liquid 2-and 4-TFMB's.

The assignments in Table 1 and Table 2 were proposed by the help of the references (Sert et al. 2008, Itoh 2004). From both the figures and tables it can be said that the most characteristic bands of the bulk liquid 2-and 4-TFMB's are also observed for their adsorbed forms on the zeolites.

The ring stretching and the CH bending vibrations of the adsorbed 2- and 4-TFMB's do not show a considerable shift relative to those for their bulk forms. The C-CF_3 stretching vibration is observed at 1319 cm^{-1} for the adsorbed 2-TFMB and at 1324 and 1329 cm^{-1} for adsorbed 4-TFMB. These values are also very close to that of their bulk liquid forms.

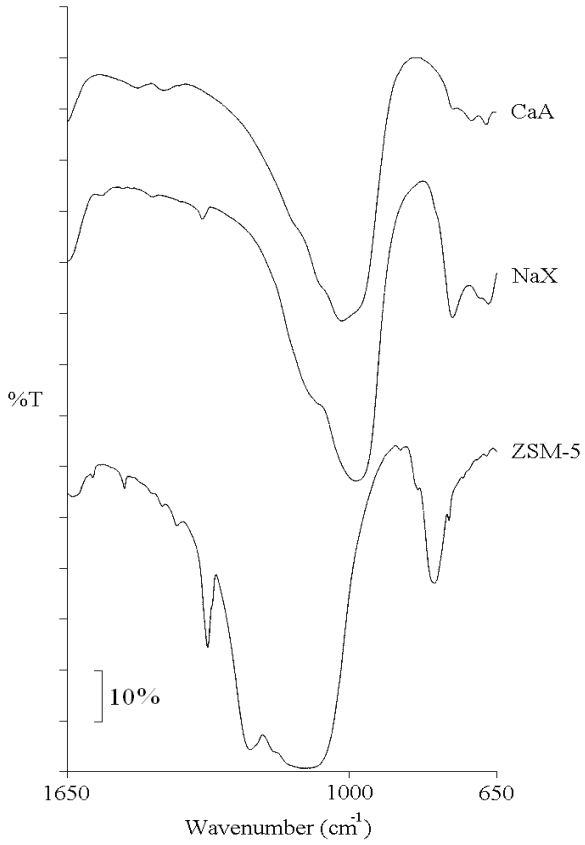

Figure 3. *Infrared spectra of 4-TFMB adsorbed on CaA , NaX and ZSM-5 zeolites*

However, the CH bending in the aldehyde (CHO) group and the C-CHO bending vibrations of the adsorbed 2-TFMB give the most considerable shift (18-22 cm^{-1}) relative to for its bulk liquid form. In addition the 672 cm^{-1} band consisting of the ring + the CF_3 in-plane bending vibrations has also an important shift (13-16 cm^{-1}). These suggest that both the aldehyde and CF_3 groups contribute to the interaction with the zeolite. This is since these two groups of 2-TFMB are close to each other. For, there is no such interaction between 4-TFMB and the zeolites. As seen in Table 2, the vibrations belong to the aldehyde and CF_3 groups of the adsorbed 4-TFMB do also not show a considerable shift like the other vibrations. The lower shifts maybe can be ascribed to a hampered interaction with the surface of the zeolites as a consequence of the higher hindrance of 4-TFMB.

Table 1. *Infrared frequencies of bulk liquid and adsorbed 2-TFMB. sh shows shoulder, w weak, m middle and s strong peaks*

Bulk liquid	Adsorbed on		Assignments
	CaA	NaX	
1601 m	1596 m	1597 sh	Ring stretching + C-H in plane bending
1584 m	1578 w	1580 sh	Ring stretching + C-H in plane bending
1490 w	1497 sh	1501 w	Ring stretching + C-H in plane bending
1455 w	-----	1466 sh	C-H in plane bending
1417 s	1406 s	1406 m	C-H in plane bending in the CHO
1319 s	1319 s	1319 m	C-H in plane bending + C-CF_3 stretching
1274 m	1273 m	-----	C-H in plane bending
1164 m	1176 w	1177 sh	C-H in plane bending + C-CHO stretching
1080 wvs	1082 sh	1084 sh	C-H in plane bending + Ring stretching
1058 vs	1054 sh	-----	C-H in plane bending + Ring in plane bending
851 w	849 w	853 sh	C-H out of plane bending
770 s	748 s	752 s	C-CHO in plane bending + Ring in plane bending + CF_3 in plane bending
672 m	685 sh	688 sh	Ring in plane bending + CF_3 in plane bending
594 w	598 sh	-----	Ring out of plane bending + CF_3 out of plane bending

Table 2. *Infrared frequencies of bulk liquid and adsorbed 4-TFMB. sh shows shoulder, w weak, m middle and s strong peaks*

Bulk liquid	Adsorbed on			Assignments
	CaA	NaX	ZSM-5	
1617 w	1618 sh	-----	1619 w	Ring stretching + C-H in plane bending
1586 m	1573 m	-----	1589 w	Ring stretching + C-H in plane bending
1513 s	1516 w	1522 sh	1516 m	Ring stretching + C-H in plane bending
1424 m	1431 w	1421 m	1427 w	C-H in plane bending
1389 s	-----	-----	1396 w	C-H in plane bending in the CHO
1323 vs	1329 m	1324 sh	1324 s	C-H in plane bending + C-CF_3 stretching
1310 w	1302 sh	-----	-----	C-H in plane bending
1175 s	1171 sh	-----	1174 sh	C-H in plane bending + C-CHO stretching
1060 vs	1066 w	1061 sh	-----	C-H in plane bending + Ring in plane bending
960 w	-----	964 sh	-----	C-H out of plane bending
866 w	872 sh	873 sh	875 w	C-H out of plane bending
758 s	752 s	-----	762 w	C-CHO in plane bending + CF_3 in plane bending
728 w	-----	-----	729 w	C-H out of plane bending + Ring out of plane bending
672 m	667 m	-----	674 w	Ring in plane bending + CF_3 in plane bending

Conclusion

From the results above we have concluded that both the aldehyde and CF_3 groups of the adsorbed TFMB's contribute together to the interaction with the zeolites when these two groups of the molecules are close to each other. Otherwise, such interaction does not come out.

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