An IR Study of Benzoyl Chloride Adsorbed on KA, NaA, and CaA Zeolites

B. Bardakçı and Semiha Bahçeli

Department of Physics, Faculty of Arts and Sciences, Süleyman Demirel University, 32260 Isparta, Turkey

Reprint requests to Dr. S. B.; E-mail: bahceli@fef.sdu.edu.tr

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Infrared spectroscopy has been used to investigate the adsorption of liquid benzoyl chloride on A-type zeolites. The data show that at room temperature the Fermi resonance phenomenon occurs in the adsorption on KA, NaA and CaA zeolites which are little acidic aluminosilicates.

Key words: IR; Benzoyl Chloride; Fermi Resonance; A-type Zeolites.

1. Introduction

Benzoyl chloride is a highly reactive acyl halide and is therefore used as benzoylation agent. The benzoylation of various acidic zeolites has given information about their structural, chemical and catalytic characteristics [1 – 3]. Recently, the vibration of benzoyl chloride in the liquid and vapour phase, adsorbed on the NaY-FAU zeolite, was studied [4]. The infrared frequencies of liquid benzoyl chloride have been reported by Rasmussen and Brattain [5]. They have observed two bands at 1773 and 1736 cm^{-1} in the double bond region, which differ from those of other carboxylic acids. Much more detailed vibrational studies of benzoyl chloride revealed that the mentioned bands were the C=O streching vibration at 1774 cm^{-1} and the overtone vibration at 1733 cm^{-1} of ν(C–Cl) ($2 \cdot 872$ cm^{-1}), which was assigned to the Fermi resonance phenomenon [6, 7].

In the following we present an IR study of liquid benzoyl chloride adsorbed on A-type zeolites.

2. Experimental

The synthetic zeolites KA (type 3A), NaA (type 4A), and CaA (type 5A) were obtained from the Aldrich Chemical Company. The unit cell contains

$$M_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O,$$

where M = K, Na and Ca. Benzoyl chloride (C_6H_5COCl) (Merck, 99%) was used without purification. As for the preparation of the samples, the mentioned zeolites were activated at 623 K for 4 h, and then 1 g of each zeolite was placed into 40 ml of liquid benzoyl chloride. After stirring and storing for 24 h, the mixtures were filtered and washed twice with diethyl ether and then filtered again and dried at room temperature.

The samples were compressed into self-supporting pellets and introduced into an IR cell equipped with KBr windows. The IR measurments at room temperature were performed on a Perkin-Elmer BX FT-IR (Fourier Transformed Infrared) spectrometer at a resolution of 4 cm^{-1} in the transmission mode.

3. Results and Discussion

The IR spectra of benzoyl chloride adsorbed on KA, NaA, and CaA zeolites are given in Figs. 1, 2 and 3, respectively. The data are summarized in Table 1.

For the assignments of the infrared vibrational frequencies of bulk benzoyl chloride we refer to [4, 5, 8]. As we mentioned in the introduction, the characteristic vibrational bands of bulk benzoyl chloride are ν(C=O) and ν(C–Cl) stretching bands at 1774 cm^{-1} and the band called Fermi resonance phenomenon at 1733 cm^{-1}, which is twice the C–Cl stretching vibration band at 872 cm^{-1} [4]. The former bands of benzoyl chloride adsorbed on A-type zeolites are observed as medium bands at 1787 cm^{-1} in the higher frequency region. The Fermi resonance bands of benzoyl chloride adsorbed on KA, CaA, and NaA zeolites arise at 1725 cm^{-1}, 1727 cm^{-1} and 1725 cm^{-1}, respectively, and are shifted to lower frequencies. On the other hand, the C–Cl streching vibration band at 872 cm^{-1} for bulk benzoyl chloride is observed as a broad weak band at 945 cm^{-1} for benzoyl chloride adsorbed on KA zeo-

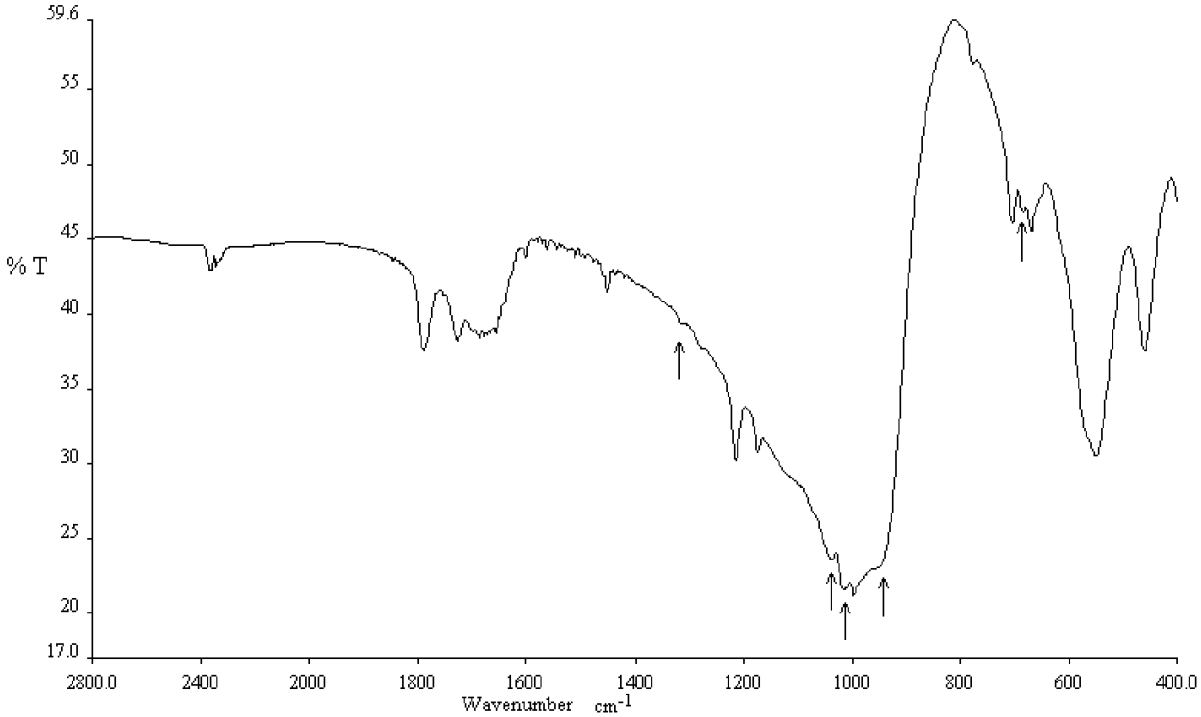

Fig. 1. Infrared spectrum of benzoyl chloride adsorbed on KA zeolite.

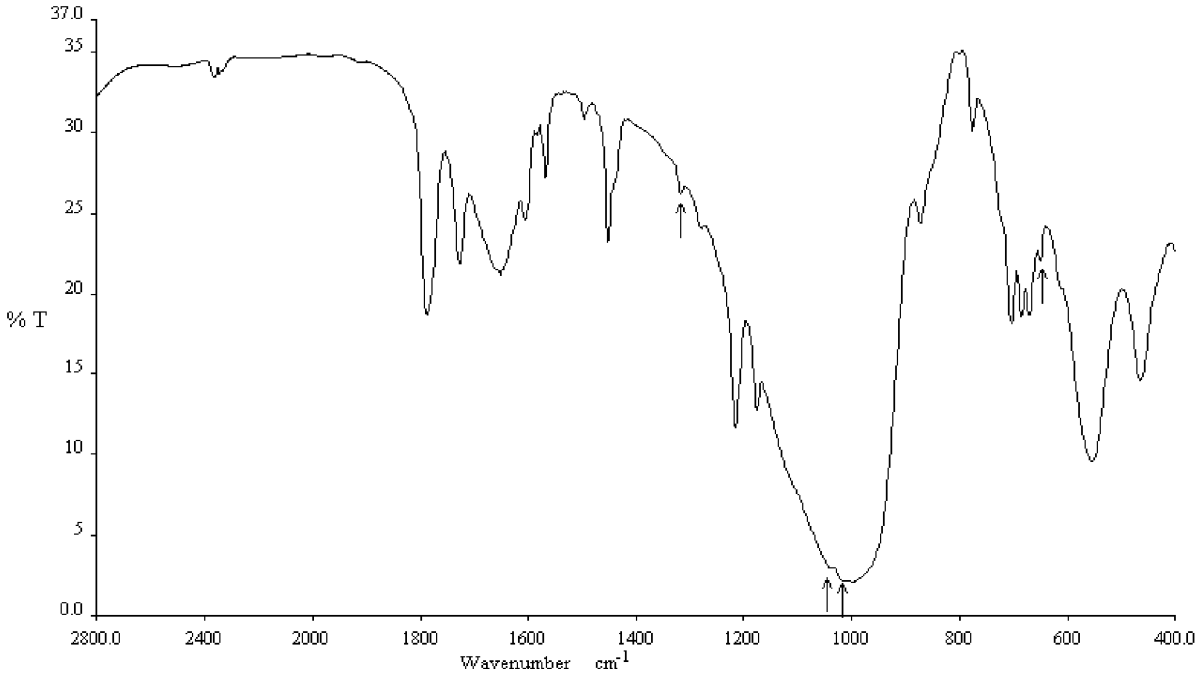

Fig. 2. Infrared spectrum of benzoyl chloride adsorbed on CaA zeolite.

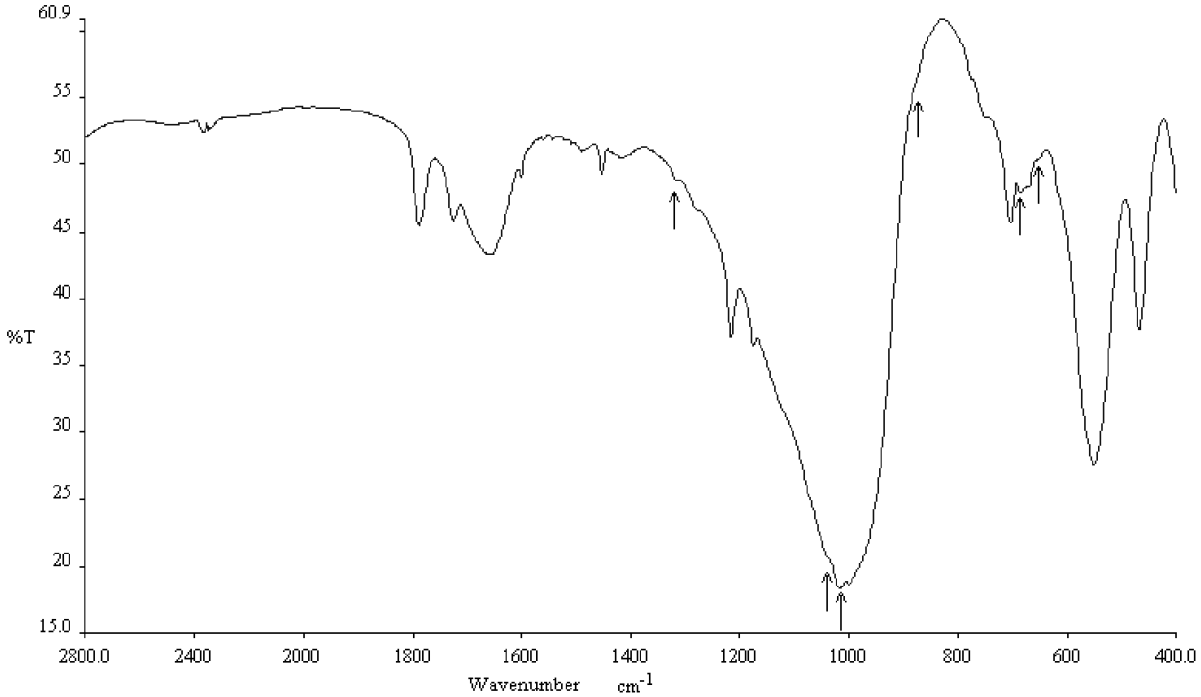

Fig. 3. Infrared spectrum of benzoyl chloride adsorbed on NaA zeolite.

Table 1. The IR frequencies (cm^{-1}) of liquid benzoyl chloride and adsorbed bezoyl chloride on KA, CaA and NaA zeolites.

Benzoyl chloride	Assignment	Benzoyl chloride adsorbed on KA	NaA	CaA
1774 s	ν(C=O)	1787m	1787m	1787m
1733 s	ν(C–Cl)	1725m	1727m	1725m
1595 s	ν(Ph–C)	1599w	1605w	1599w
1582 s	ν(Ph–C)		1567w	
1450 s	ν(Ph–C)	1451m	1451m	1451m
1316 m	C–H bend	1317w	1316w	1316w
1205 s	C–H scissor	1214m	1214m	1214m
1175 s	C–C out-of-plane-scissor	1173w	1174w	1173w
1038 m	C–C out-of-plane-scissor	1039w	1041w	1039sh
1016 s	C–C out-of-plane-scissor	1017w	1017w	1015w
872 s	ν(C–Cl)	945bsh	873w	872sh
774 s	ν(C–Cl)	777w	776w	778w
684 m	ν(C–Cl)	685w	685w	684w
670 s	ν(C–Cl)	668w	670w	669w
649 s	ν(C–Cl)		650w	650w

s, strong; m, medium; w, weak; bsh, broad shoulder; sh, shoulder; ν, stretching.

lite (shown with an arrow in Fig. 1) and at 872 cm^{-1} (shoulder band) and 873 cm^{-1} (weak band) for adsorbed benzoyl chloride on CaA and NaA zeolites (denoted with arrows in Figs. 2 and 3), respectively.

As seen in Table 1, the C–H bending vibration mode at 1316 cm^{-1}, the C–C out-of-plane-scissor mode at 1038 cm^{-1} and 1016 cm^{-1}, and the C–Cl stretching vibration band at 684 cm^{-1} and 649 cm^{-1} for bulk benzoyl chloride are observed in the IR spectra of adsorbed benzoyl chloride on 3A, 4A, and 5A zeolites as weak bands at 1317 cm^{-1} and 1316 cm^{-1}, 1039 cm^{-1} and 1041 cm^{-1} and as the shoulder band at 1039 cm^{-1} and as the weak bands at 1015 cm^{-1} and 685 cm^{-1}, 684 cm^{-1} and 650 cm^{-1} which are all denoted with arrows on Figs. 1, 2 and 3, respectively.

In fact these frequency shifts to lower and higher regions show the existence of adsorption of liquid benzoyl chloride on the zeolites. The reasons of adsorption on the zeolites can be explained by considering the hydroxyl groups, structural OH groups and non-acid silanol (SiOH) hydroxyl groups, in zeolites [9].

As a conclusion we can state that the crucial point is that the Fermi resonance phenomenon was observed in the liquid phase spectra of benzoyl chloride adsorbed on A-type zeolites as the less acidic zeolite than NaY-FAU and it is obviously confirmed that there is no influence of the acidity of the zeolites as the adsorbents [10].

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