Adsorption of Trimethyl Phosphite on H-KA, H-NaA, H-CaA and H-NaX Zeolites: an IR Study

E. Çiçek, B. Bardakçı, F. Ucun, and S. Bahçeli

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

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

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Infrared spectroscopy has been used in adsorption studies of trimethyl phosphite (TMP) on the hydrogen (H) form of the A-type and 13X zeolites. Infrared spectra of H-zeolites, except H-KA, show that TMP reacts rapidly with silanol hydroxyls on their surfaces and gives rise to form product molecules such as $SiOCH_3$ and liquid dimethyl phosphite. The unaccomplished adsorption on the H- KA zeolite has been attributed to the occurence of stable KOH hydroxyls with not-exchanged K cations instead of SiOH hydroxyls on this zeolite.

Key words: IR; TMP; H-KA; H-NaA; H-CaA and H-NaX Zeolites.

Introduction

The catalytic properties of zeolites can be understood by studying the adsorption characteristics of the reactant, intermediate and product molecules formed on their surface [1 – 2]. On the other hand, in the past decade the adsorption of trimethyl phosphite (TMP) as an organophosphorous compound on some zeolites has been reported to be a selective molecule for the characterization of acid sites of zeolites [3 – 5]. Nyquist gave the vibrational modes of bulk TMP, and recently Gay et al. investigated the adsorption of TMP on silica by using the magic angle spinning nuclear magnetic resonance (MAS NMR) and infrared (IR) spectroscopy [6 – 7].

However, in our previous work we have investigated the infrared spectra of TMP adsorbed on NaY zeolite, and we have concluded that the chemisorption results solely from the interaction between TMP and non-acidic (silanol) hydroxyls on the surface of an NaY zeolite [8]. But we have not obtained similar results for the adsorption of TMP on the surface of activated A- and X-type zeolites, and therefore we concluded that the mentioned type zeolites do not have any silanol hydroxyl groups on the zeolitic surfaces.

In the present study we report the IR spectra of TMP adsorbed on hydrogenated H- forms of 3A, 4A, 5A and 13X zeolites.

Experimental

The synthetic zeolites KA (type 3A), NaA (type 4A), CaA (type 5A) and NaX (type 13X) used in this work were purchased from the British Drug House (BDH).

The unit cell of the zeolite NaA consists of

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O.$$

The zeolites KA and CaA are the potassium- and calcium- exchanged forms of the zeolite NaA, and the unit cell of the zeolite NaX consists of

$$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264H_2O$$

[2, 9 – 10]. Trimethyl phosphite (Sigma, 97%) and NH_4Cl (Riedel - de Haen, 99,5% and dehydrated) were used as bought.

For NH_4^+ exchanged zeolite, the water in the pores was evaporated at 623 K during 4 hours, and then 1 g of zeolite was placed into an aqueous solution of NH_4Cl of 5.10^{-3} M. After stirring and storing for 24 h, the solutions were filtered and kept at 823 K during 4 h. Then, for TMP adsorption 1 g of the protonated form of each zeolite was placed into 20 cm^3 of liquid TMP. After stirring and storing for 24 h, the mixture was filtered and dried at room temperature. The sample was compressed into a self-supporting pellet and introduced into an IR cell equipped with KBr windows. The

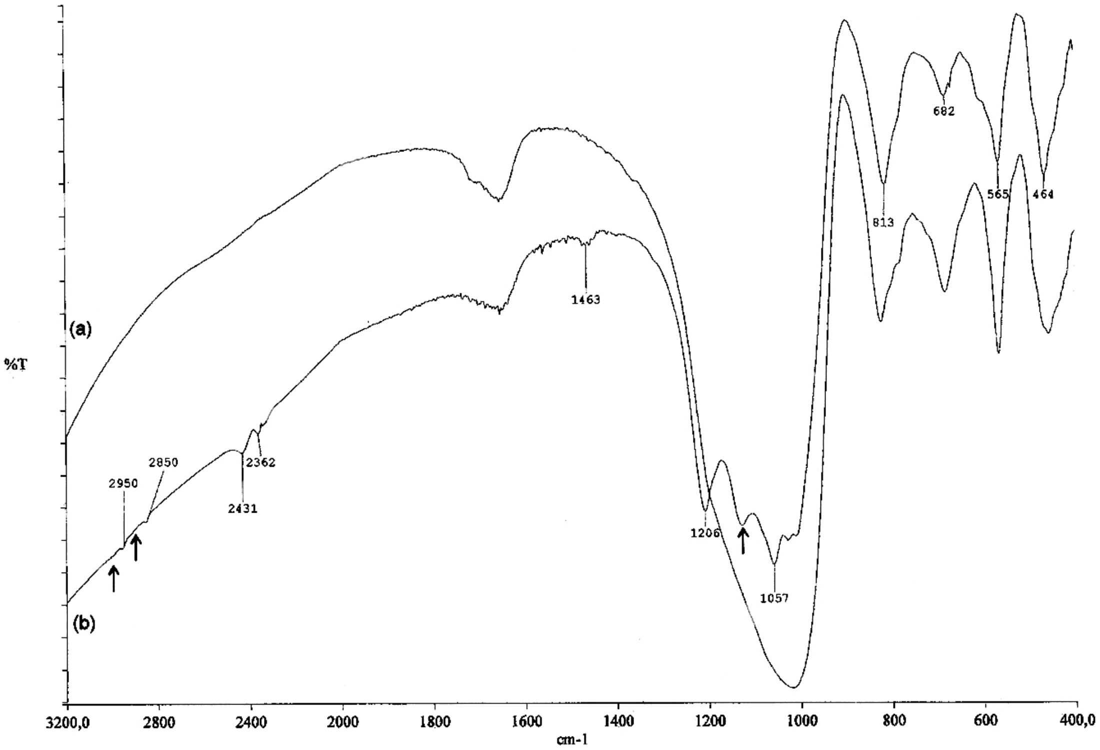


Fig. 1. At room temperature (a) IR spectrum of pure H-NaA zeolite, (b) IR spectrum of TMP adsorbed on the H-NaA zeolite.

IR measurements 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.

Results and Discussions

IR spectra of the H-forms of 4A, 5A and 13X zeolites used in this study are given in Figs. 1(a), 2(a) and 3(a), respectively. IR spectra of TMP adsorbed on the H-NaA, H-CaA and H-NaX zeolites are exhibited in Figs. 1(b), 2(b) and 3(b), respectively. IR spectral data for each sample with adsorbed TMP are listed in Table 1.

In Fig. 1(b), the bands at 2850 cm^{-1} and 2950 cm^{-1} are the methyl (CH_3) stretching modes of DMP and the broad band at 1463 cm^{-1} is the CH_3 bending mode [11]. A band between 2400 cm^{-1} and 2700 cm^{-1} can be indicative of the presence of the species contained P-H bond [12]. Therefore the bands at 2431 cm^{-1} and 2362 cm^{-1} can be assigned to the P-H stretching mode of DMP. On the other hand, very weak bands around 3000 – 2900 cm^{-1} (denoted with arrows) can be assigned to the existence of $SiOCH_3$ called chemisorption product on the zeolite [13]. As a matter of fact this band interval was attributed to the adsorptions of trimethyl phosphine on SiOH groups in HZSM-5 zeolite by Rumplayr et al. [5]. The strong bands at 1206 cm^{-1} and 1057 cm^{-1} are the P=O stretching mode and P-O stretching mode of DMP, respectively [14 – 15]. Furthermore, the new band at 1127 cm^{-1} (shown with an arrow) can be interpreted as the overtone band (396 + 734 = 1130) of unreacted TMP which

Table 1. Group frequencies (cm^{-1}) for TMP adsorbed on H-Na, H-CaA and H-NaX.

Frequencies adsorbed on			
H-NaA	H-CaA	H-NaX	Assignment
2950 (w)	2962 (w)	2963 (w)	$^{\nu}\text{symCH}_3^{(\text{DMP})}$
2850 (w)	2856 (w)	2854 (w)	$^{\nu}\text{asymCH}_3^{(\text{DMP})}$
2431 (m)	2431 (s)	2454 (b)	P-H stretching
2362 (m)			P-H stretching
1463 (b)	1464 (m)	1464 (b)	$^{\delta}\text{asym.CH}_3^{(\text{DMP})}$
1206 (s)	1209 (m)	1185 (w)	P=O bending
1127 (m)	1123 (b)		$396 + 734 = 1130$
1057 (s)	1055 (m)		P-O stretching

b = broad, m = medium, s = strong, w = weak.

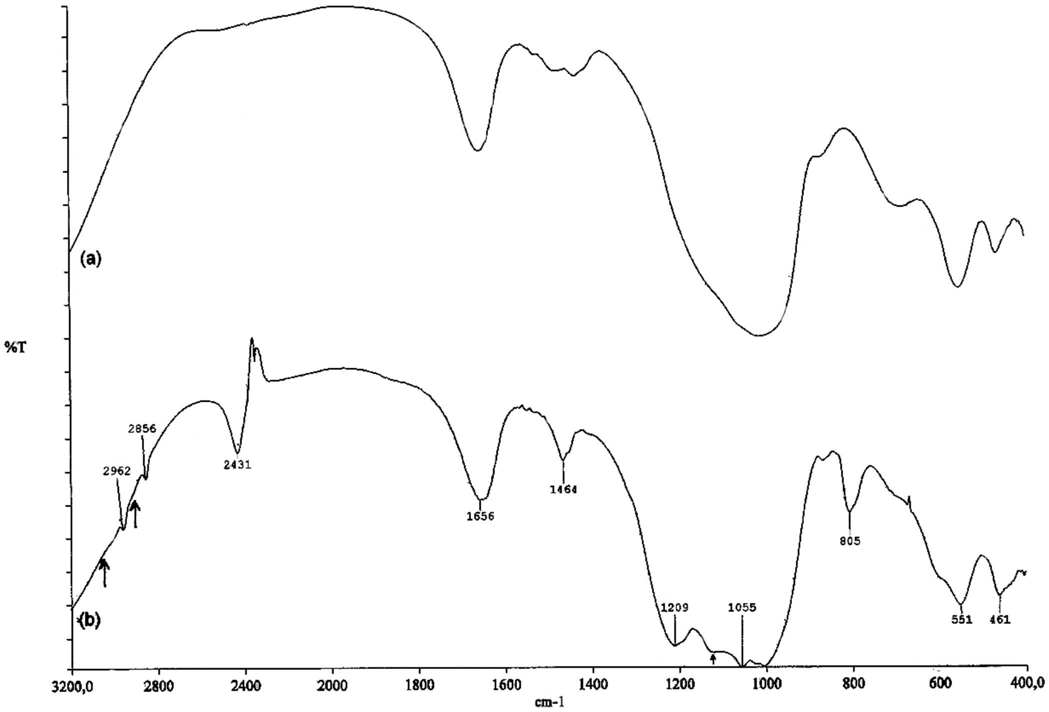
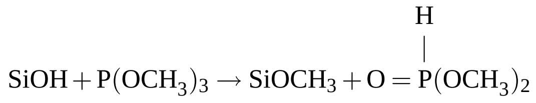


Fig. 2. At room temperature (a) IR spectrum of pure H-CaA zeolite, (b) IR spectrum of TMP adsorbed on the H-CaA zeolite.

is in excess [6]. In Fig. 2(b), IR spectrum of TMP adsorbed on H-CaA zeolite can be interpreted by considering the spectral data in Fig. 1(b). It can be easily seen from Table 1, the bands for the TMP adsorbed on H-CaA zeolite have almost the same frequencies as former sample except the absence of the band at 2362 cm^{-1} and an extra band at 805 cm^{-1}. The strong band at 805 cm^{-1} in Fig. 2(b) can be considered as a known mode of $SiOCH_3$ which is shifted from 850 cm^{-1} to 805 cm^{-1} in frequency [7]. IR spectrum of TMP adsorbed on H-NaX zeolite in Fig. 3(b) exhibits almost the same vibration modes as those of TMP adsorbed on H-NaA and H-CaA zeolites. But the band at about 1055 cm^{-1} which denotes the P-O stretching mode is not appeared in this sample.

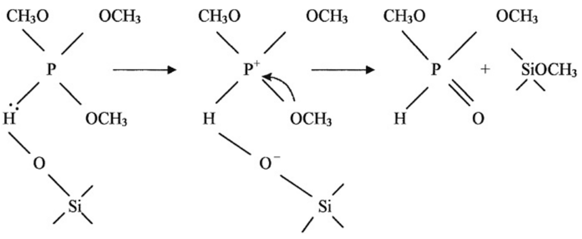
We can conclude that the experimental results of IR studies show that the surface silanol hydroxyl groups contribute to the adsorption of TMP on the zeolites. The formation of these non-acidic hydroxyls on the surface of zeolites can be explained as follows. When NH_4^+ exchanged zeolites are kept at 823 K the NH_4^+ ions decompose to the NH_3 and H^+ ions. Thus the sites containing H^+ or indirectly acidic sites are established in the zeolites. Since the H^+ ion will accept an electron the non-acidic silanol hydroxyl groups (SiOH) are formed on the zeolitic surfaces. TMP reacts rapidly with these silanol hydroxyls on the surface of zeolites to give $SiOCH_3$ as a chemisorbed product and liquid dimethyl phosphite (DMP).

The conversion between TMP and silanol groups can be considered in the followings:



$$SiOH + P(OCH_3)_3 \rightarrow SiOCH_3 + O = \overset{\overset{\displaystyle H}{|}}{P}(OCH_3)_2$$

or more explicitly,



On the other hand, the infrared spectrum of TMP adsorbed on the H-KA zeolite has not been observed. This can be interpreted as follows. The non-exchanged

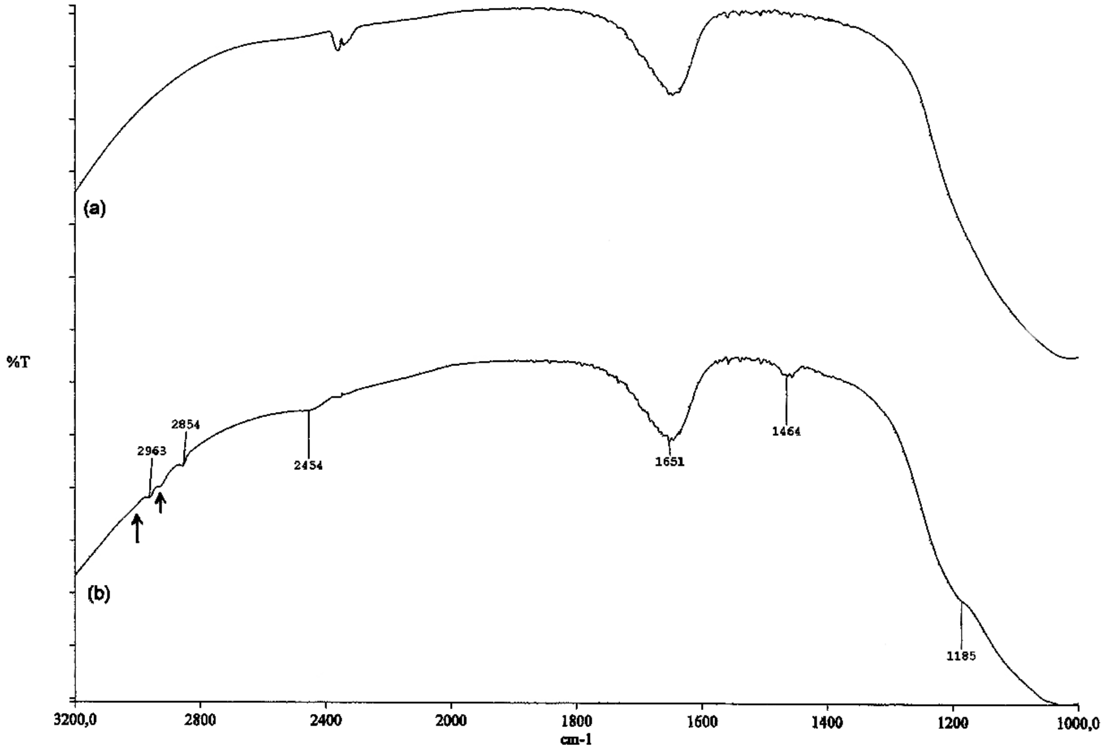


Fig. 3. At room temperature (a) IR spectrum of pure H-NaX zeolite, (b) IR spectrum of TMP adsorbed on the H-NaX zeolite.

K cations in the hydrogenated 3A zeolite react with H^+ ions and give rise to the formation of KOH hydroxyls instead of SiOH hydroxyls on the zeolitic surface. For this reason, the adsorption of TMP on the mentioned zeolite has not been verified.

Acknowledgements

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