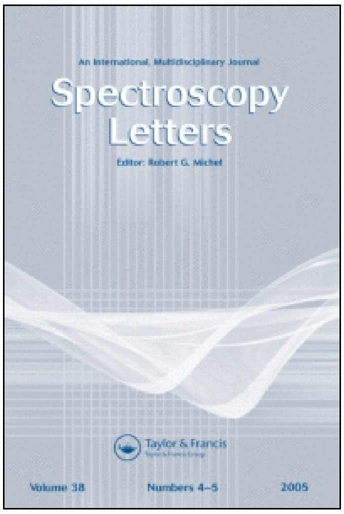

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AN IR STUDY OF TRIMETHYL PHOSPHITE ADSORBED ON NaY ZEOLITE

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AN IR STUDY OF TRIMETHYL PHOSPHITE ADSORBED ON NaY ZEOLITE

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ABSTRACT

Infrared spectroscopy has been used to investigate the adsorption of trimethyl phosphite (TMP) on the NaY zeolite. The obtained spectrum indicates that at room temperature TMP reacts rapidly with the non-acidic (silanol) hydroxyls on the surface of the zeolite to give $SiOCH_3$ as a chemisorbed product and liquid dimethyl phosphite (DMP).

Key Words: Infrared spectroscopy; Trimethyl phosphate; TMP; NaY zeolite

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INTRODUCTION

The vibrational spectra of the bulk trimethyl phosphite (TMP) as an organophorous compound have been reported by Nyquist[1,2]. Recently, the magic angle spinning nuclear magnetic resonance (MAS NMR) and infrared (IR) studies of trimethyl phosphite adsorbed on silica were presented by Gay et al[3]. They have shown that at room temperature TMP reacted rapidly with surface silanol groups and gave $SiOCH_3$ as a chemisorbed product and liquid dimethyl phosphite (DMP).

On the other hand, it is a well-known fact that an understanding of the catalytic properties of zeolites is based on a knowledge of the adsorption characteristics of reactant, intermediate and product molecules[4,5]. For this purpose, in our work we have used the NaY zeolite as an adsorbent of the TMP.

EXPERIMENTAL

The substrate NaY sample having a general unit cell content of[5]

$$Na_{56}(AlO_2)_{56}(SiO_2)_{136}250H_2O$$

was purchased from the Aldrich. The Si/Al ratio of the sample is 3. Trimethyl phosphite (Sigma, 97%) was used without any purification. The preparation of the sample for infrared spectroscopy examination is as follows. The NaY zeolite was activated at 623 K for 4 h, and then 1 g of 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 temparature. Sample was compressed into self-supporting pellet and introduced into an IR cell equipped with KBr windows. IR spectra were recorded at room justified temperature on a Perkin-Elmer BX FT-IR (Fourier Transformed Infrared) spectrometer with a resolution of 4 cm^{-1} in the transmission mode.

RESULTS AND DISCUSSION

IR spectra are given in Fig. 1. Upper and lower lines in the Fig. 1 show the IR spectra of TMP adsorbed on the NaY zeolite and pure NaY zeolite, respectively. The obtained data from IR spectrum are summarized in Table 1. In IR spectrum, the bands at 2858 cm^{-1} and 2966 cm^{-1} are mainly

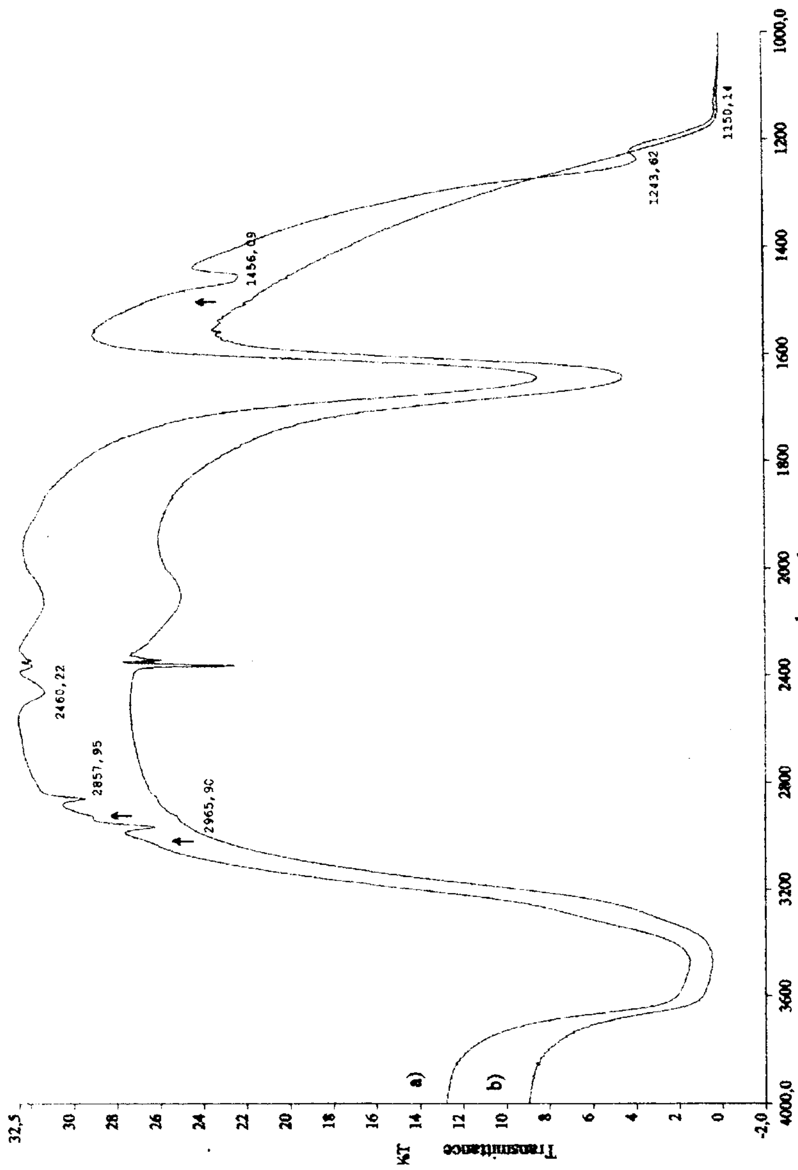


Figure 1. a) IR spectrum of TMP adsorbed on the NaY zeolite, b) IR spectrum of pure NaY zeolite at room temperature.

Table 1. Vibration Modes and Frequencies of Bulk TMP and TMP Adsorbed on NaY Zeolite

Frequencies (cm^{-1}) bulk TMP[1]	Assignment	Frequencies (cm^{-1}) for TMP Adsorbed on NaY	Assignment
2990	$\nu_{asym}CH_3$	2858 (m)	$\nu_{asym}CH_3$ (DMP)
2949 and 2939	$\nu_{sym}CH_3$	2966 (m)	$\nu_{sym}CH_3$ (DMP)
1459	$\delta_{asym}CH_3$	2460 (b)	P-H streching
1436	$\delta_{sym}CH_3$	1456 (s)	$\delta_{asym}CH_3$ (DMP)
		1244 (w)	P=O streching
		1150 (w)	P-O streching

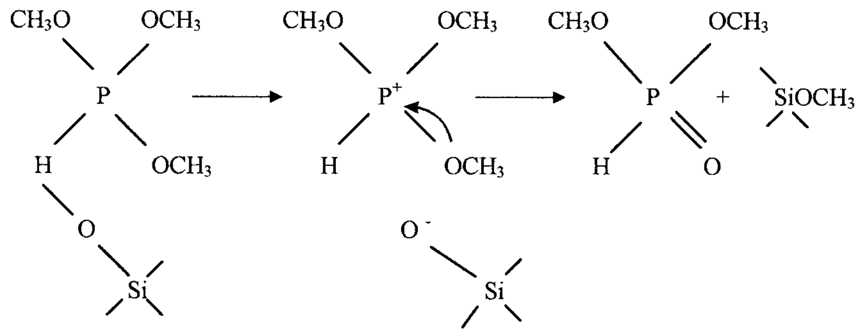
m = medium, b = broad, s = strong, w = weak.

the CH_3 (methyl) streching modes of DMP and the strong band at $1456\,cm^{-1}$ can be assigned as the CH_3 bending mode[6]. The broad band at $2460\,cm^{-1}$ is the P-H streching mode of DMP since a band between $2400\,cm^{-1}$ and $2700\,cm^{-1}$ can be indicative of the presence of the species contained P-H bond[2]. Furthermore, very weak bands which are denoted with the arrows at the interval $2800–3000\,cm^{-1}$ and $1470\,cm^{-1}$ in Fig. 1 can identify the existence of $SiOCH_3$ called chemisorption product on NaY zeolite[7]. The other two bands at $1244\,cm^{-1}$ and $1150\,cm^{-1}$ are the P=O and P-O streching vibration modes of DMP, respectively[6,8].

As we know that, the Bronsted acidity of zeolites arises from the presence of accessible hydroxyl groups associated with framework aliminium and this kind of hydroxyl groups is called ‘‘structural or bridging hydroxyls’’. Another hydroxyl groups are formed on the surface of zeolite crystallites and crystal defects sites. This sort of hydroxyl groups is called the non-acidic or silanol hydroxyls. These are well-known from other silicates and silica itself. The results of IR studies confirm that the surface silanol groups contribute to the adsorption of TMP on the NaY zeolite. The reaction between TMP and the non-acidic hydroxyl (silanol) can be shown as

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

or in an explicit chemical structure form



As a result we conclude that at room temperature TMP reacts rapidly with SiOH groups on the surface of the NaY zeolite and gives chemisorbed $SiOCH_3$ and H-bonded DMP.

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