

Fourier Transformation Infrared Spectroscopic Studies of Acidity of NaH-13 X Zeolites

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Abstract

Fourier transformation Infrared spectroscopy (FTIR) has been used to characterize and measure the concentration of acid sites (Si-OH-Al groups) in NaH-13 X Zeolites. Ion exchange was followed by dealumination to get (28, 40, 65, 85.8 and 97.5 Wt. %) of NaH-13 X Zeolites samples. The conclusion of homogeneity of OH groups was obtained by analysis of Fourier transformation infrared spectroscopy absorption bands of OH groups after adsorption and desorption of Ammonia. It found that there were different acid sites on a broader absorption (3,800-3,000 cm^{-1}) corresponds to hydroxyl groups of the less acidic Brønsted acid sites approximately at 3464 cm^{-1} and the more acidic at 3441 cm^{-1} and Lewis acid sites was found at 1636 cm^{-1} which is few and weak acid sites. It can be conclusion that concentrations of OH groups increased with increasing the exchange degree and delamination. The concentration of acid sites in samples were calculated from stretching frequencies and extinction coefficients of OH bands, also the frequency shift $\Delta\nu_{\text{OH}} = 23 \text{ cm}^{-1}$ which was due to the hydrogen bonding of OH groups with ammonia in 97.5 % NaH-13 X Zeolites. Knowing the acidity of catalyst is important for the reactions which required acidic surface.

Keywords: Brønsted Acidity, FTIR, Ammonia Adsorption, Acidity of Zeolites.

1. Introduction

Zeolites and other microporous materials are used as catalyst supports and as catalysts [1]. However, because of a number of desirable properties, Zeolites are used widely as catalysts in petrochemical industry, these properties are: (1) presence of Brønsted acid sites (BAS) that act as active sites in catalysis (2) they have crystalline structures with the pores (channels) of molecular dimensions, and (3) high thermal stability. Also there are a large number of existing structures for Zeolites which allows selection of the suitable channels for particular target molecules and reactions. Only smaller molecules than zeolite channels can move through the channels and react (reactants) or escape (products). The shape-selectivity of molecules in the Zeolite catalysts

make it very important in the exploitation of the industrial processes [2]. Faujasitic zeolites have channels of about 8 Å diameter connecting by 13 Å diameter (super cages) in three dimensional networks [3]. There are Si – OH groups (silanols) in Zeolites which can occur at the external surface of crystals and may be occur at intra crystalline lattice defects which may influence catalytic phenomena [1]. The Brønsted acidity in zeolites (aluminosilicates) is due to OH bridged between Si and Al of the framework. The acidity of zeolites governs their activity, that make many studies of the acidity, the strength of the acidic sites, determination of the nature and the number of acid sites. Among the main methods used, Fourier transformation infrared spectroscopy (FTIR) appears very fruitful [4]. The infrared spectrum of a simple molecule arises as a result of the vibrations of the atoms within the molecule, the symmetry and bond strengths of the molecule as a whole determine the number and frequencies of the vibrations. When a simple molecule is adsorbed the "one-sided" surface forces exerted by a catalytic material must cause a change in asymmetry of the molecule, any quantities measure of this change can be directly related to the nature of the adsorption [5]. Beran and Schröder et al. [5] have proved the acid strength of bridging Si-OH-Al groups depends on, first the geometrical factor and secondly on the chemical factor also Datka and Gil [5] were studied heterogeneity of OH groups in faujasites. They found that the Si-OH-Al groups were homogeneous in Na-HX zeolite and heterogeneous in Na-HY zeolite from experiments of pyridine sorption and desorption, also they proved that in the case of Na-H-X zeolites only one band at 3478 cm^{-1} ($\Delta\nu = 182 \text{ cm}^{-1}$) is present, whereas three sub maxima at 3320, 3380 and 3420 cm^{-1} exist in Na-HY. The acid properties of Na-HX were modified by varying the Na/H exchange degree, partial dehydroxylation, and by delamination. The acidity of Na-H-mordenites was studied by numerous authors using infrared spectroscopy, Temperature Programmed Desorption (TPD) of Ammonia microcalorimetry, and adsorption isotherms. Known zeolites contain either homogeneous, weakly acidic hydroxyls (Na-HA,

Na-HX) or more acidic but heterogeneous ones (HZSM-5, HY, H-Beta, H-mordenite). No zeolite is known with strongly acidic homogeneous OH groups [6]. The micro calorimetric studies of ammonia adsorption suggested homogeneity of (Na-HA, Na-HX): the adsorption heat was constant until all the OH groups were neutralized [7]. Ammonia has been used as a probe molecule in infrared spectroscopy. The intensity of OH depends on the concentration of OH and the extinction coefficient [8]. Na-H-13X may contain both Brønsted and Lewis acid sites, practically all studies were made using pyridine as the probe molecule. But pyridine cannot reach acid sites in narrow channels. Ammonia can penetrate all zeolite pores and provides information on the whole population of acid sites which some of them may be located in broad channels and others in narrow ones. In the present work the acid properties of Na-H-13X Zeolite were determined by Fourier transformation infrared spectroscopy techniques of ammonia sorption. Masato et. al. [9], studied the adsorption of NH₃ molecules and NH₄⁺ on ZSM-5 zeolites with different SiO/Al₂O₃ ratios by near and middle infrared spectroscopy and they concluded that the adsorption of NH₃ molecules and NH₄⁺ on ZSM-5 zeolites were successfully investigated. To prevent side – reactions, it must be decrease the acidity of the catalyst and decrease the reaction temperature [10]. Dealumination causes an increase in the acid strength [11]. Shashikant and Mariya [12], determined the concentration of Lewis and Brønsted acid sites of H-MFI Zeolites after adsorption of pyridine by FTIR spectroscopy. They studied the influence of the reaction conditions and zeolite characteristics on bio-ethanol dehydration pathways. Ammonium and protonic zeolite forms are studied by Paola and Katina; they found a linear relationship between rate constant in the etherification of HMF (5-Hydroxymethyl furfural) and the amount of Lewis acid sites and Brønsted acid sites [13]. Ying Li et al. studied the influence of Brønsted acid density and strength on the stability of H-MOR in Dimethyl ether carbonylation; they recognized Pyridine adsorption is as an efficient technique to improve stability by FTIR. They concluded that acidity strongly influences the activity and stability of modified MOR, also the stability is affected by the amount and location of acid site [14].

Acidity of zeolites must be taken into account in reactions, to prevent side reactions, it is usual to decrease the acidity of the solids and the reaction temperature. In order to solve these problems regarding the acidity (strength, number) some samples of dealuminated 13X- zeolites were prepared with different acidities and tested. The aim of this study was to determine the

concentration of Brønsted and Lewis acid sites in Na-H-13X Zeolites and their acid strength using quantitative FTIR experiments of ammonia adsorption, to prove that acidic hydroxyls (OH) in Na-H-13X Zeolites are homogeneous. Known homogeneous zeolites are weakly acidic, also to find the relation between the concentration of acidic hydroxyls and the Na/H exchange degrees.

2. Experimental work

A commercially available sodium zeolites from Fluka Company AG as synthetic crystalline zeolite type Na-13X with formula composition Ca_{4.5}. Na (AlO₂)₁₂.(SiO₂)₁₂.30H₂O (Si/Al=1.75) was used as the original zeolite table (1). Ionic-exchanged by NH₄Cl (2N) solution for (2h.) two times at 80°C was used to prepare H-13X-Zeolites. To dealuminate the exchanged zeolites different molarities (0.2, 0.3, 0.5 and 4N) of hydrochloric acid (Merck) at 80°C were used. The exchange degrees of our samples were (28, 40, 65, 85.8 and 97.5 Wt. %) (determined by Chemical analysis in the company of Geological Survey and mining) has shown in Table (2). The Fourier transformation infrared spectroscopy was taken by (FTIR-8400S-Shimadzo) spectrometer with a resolution of 2 cm⁻¹. The percentage of the sample in the KBr salt was 2-5 %. The samples were pressed into thin wafers (5-10 mg.cm⁻²) and directly activated in situ in an I.R. cell at 523K for 3 hours in a vacuum (1.10⁻³ mg.cm⁻²) then pretreated by small measured portions of dry ammonia (Linde Carbide 99.97%) at 320 K in Na-H-13X Zeolites (exchange degree 97.5%), then by an access of ammonia (the amounts of ammonia added must be larger than the amounts needed to saturate all of the acid sites) after 30 min. contact with the zeolites, in the evacuated cell. Physically adsorbed ammonia were removed by evacuation at 523K again for 3hours, only chemisorbed ammonia will remain, each ammonia molecule reacts chemically with one acid site (desorption of physically adsorbed ammonia occurs in the range of 473K-523K).

Table (1): Chemical composition and oxide formula for Na-13X zeolite.

Na-13X Zeolite	Chemical Composition Wt. %
oxide formula	Ca _{4.5} .Na(AlO ₂) ₁₂ .(SiO ₂) ₁₂ .30H ₂ O
SiO ₂	37.0
Al ₂ O ₃	36.21
Na ₂ O	10.3

Table (2): Ion exchange data for zeolites 13-X after treatment with NH₄Cl and after delamination

Zeolite 13X	Amount of Na ₂ O in the zeolite before treatment	Treatment solution	Concentration of treatment solutions	Treatment Period (hr)	Calcinations temp. °C	Exchange%
NH ₄ -X	10.3	NH ₄ Cl	2N	4	550	28
H-X		HCl	0.2N	3	550	40
H-X		HCl	0.3N	3	550	65
H-X		HCl	0.5N	3	550	85.8
H-X		HCl	4N	3	550	97.5

3. Results and Discussion

3.1. OH groups in Na-H-13X Zeolites

The FTIR spectrum of 13-X zeolite (Si/Al=1.75) before any treatment and before adsorption of ammonia is presented in (Fig.1). One distinct Si-OH-Al band at 3474cm⁻¹ which can be Brønsted acid sites can be noticed.

In Figure (2), one band appeared at 3464cm⁻¹ characteristic of ammonia bonded to Na⁺ cations (NaNH₃). The spectra of (Si-OH-Al groups) can be noticed in Figures (3), (4), (5), (6) and (7) which become shifted to lower frequencies because of hydrogen bonded with ammonia which adsorbed at 320K in Na-H-13X Zeolites. Also one I.R. band is shown at 1636 cm⁻¹ which is the characteristic of ammonia bonded with Lewis acid sites (LNH₃).

It can be noticed that before ammonia adsorption, and after the reaction of ammonia with Lewis acid sites, there are no change happened for 1636 cm⁻¹ band. That is mean Lewis acid sites (LNH₃) are very weak in Na-H-13X, 1636 cm⁻¹ band has low intensities and cannot be distinguished.

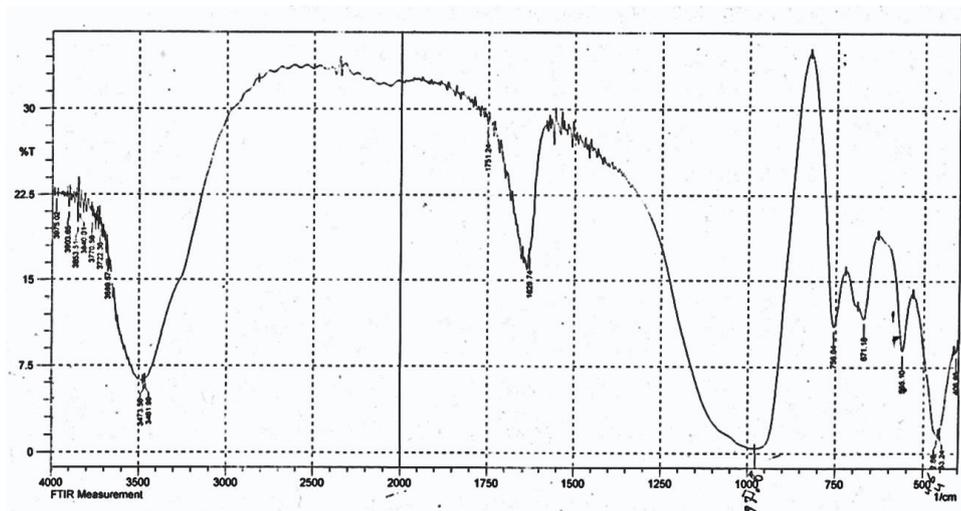


Figure (1): FTIR Spectrum of free Si-OH-Al groups in Na13X zeolite (Si/Al=1.75) before any treatments.

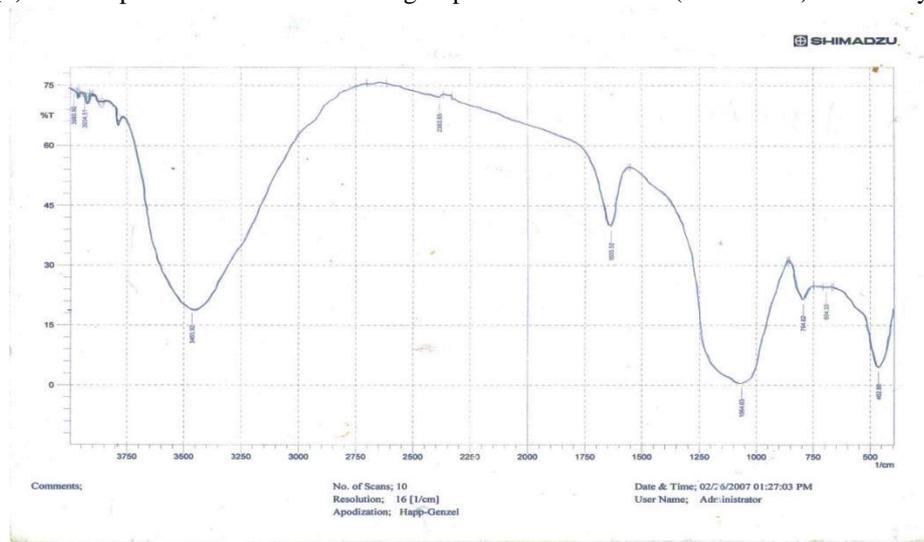


Figure (2): FTIR Spectrum of OH groups in NaH13X zeolites (28%) after Ammonia adsorption.

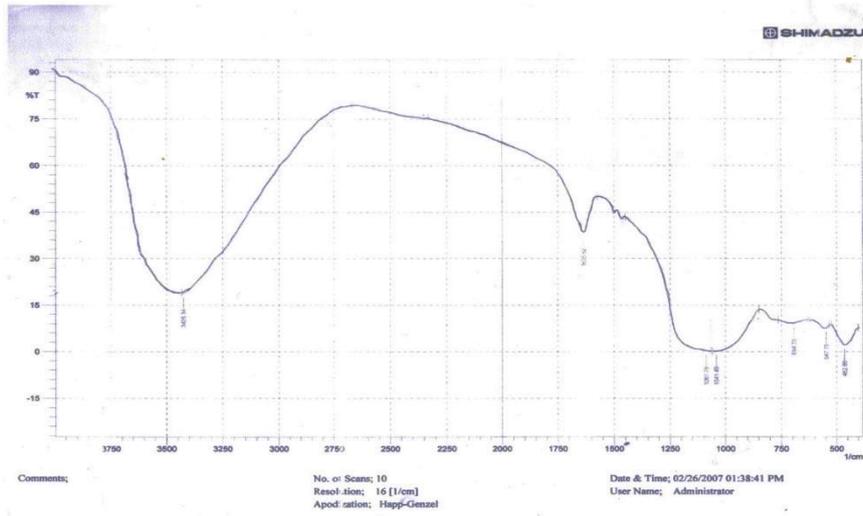


Figure (3): FTIR Spectrum of OH groups in NaH13X zeolites (40%) after Ammonia adsorption.

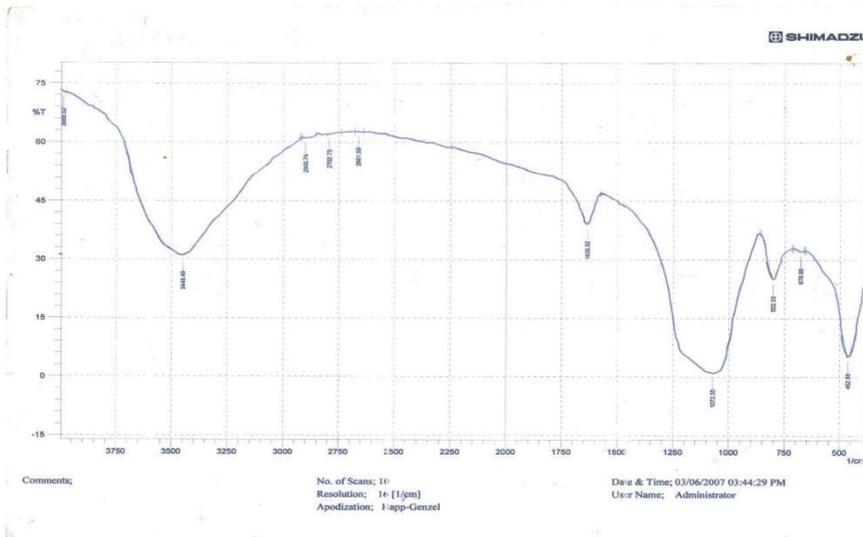


Figure (4): FTIR Spectrum of OH groups in NaH13X zeolites (65%) after Ammonia adsorption

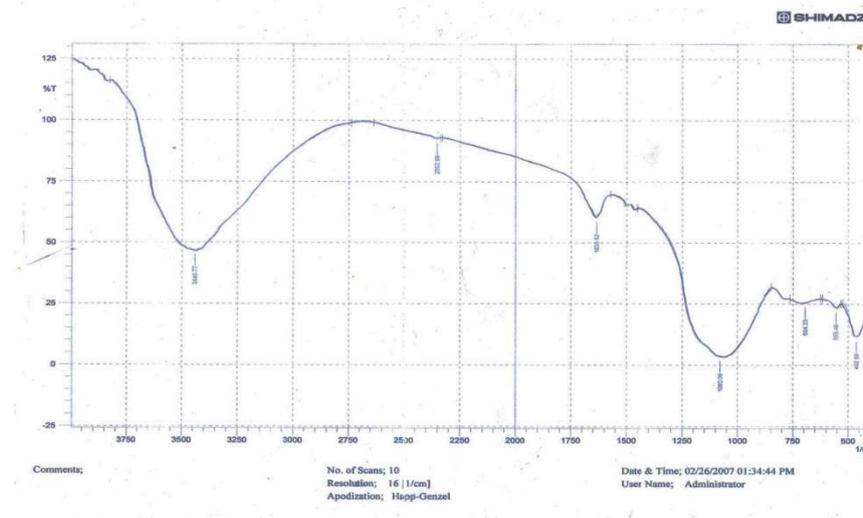


Figure (5): FTIR Spectrum of OH groups in NaH13X zeolites (85.8%) after Ammonia adsorption.

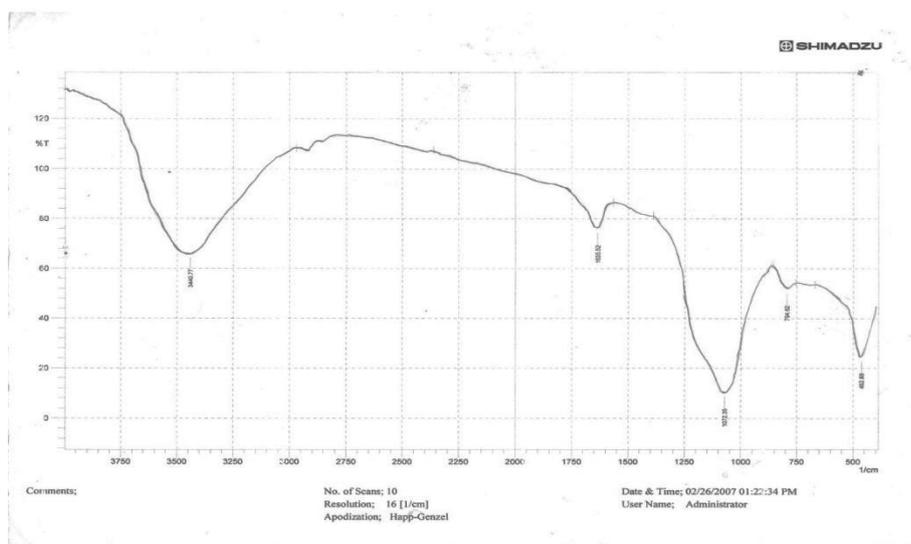


Figure (6): FTIR Spectrum of OH groups in NaH13X zeolites (97.5%) (Si/Al = 52) after Ammonia adsorption.

Figure (7) shows the relation between the amount of chemisorbed ammonia and the intensity of NH_4^+ at 1450cm^{-1} band, small portions of ammonia were adsorbed at 320 K in Na-H13X (exchange degree 97.5%) until all hydroxyls were neutralized (when the OH band disappeared), practically the intensity of the 1450cm^{-1} band increased linearly with the amount of ammonia adsorbed at 320K in Na-H13X (exchange degree 97.5%). Infrared (I.R.) spectra were recorded at each sorption step until the NaNH_3 band is absent; the slope of this line was taken as the extinction coefficient of the 1450cm^{-1} band. The value of it was approximately $0.12\text{cm}^2 \cdot \mu\text{mol}^{-1}$.

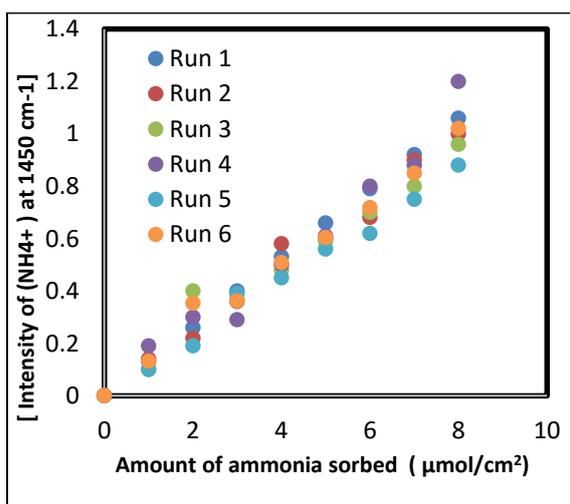


Figure (7): The relation between the intensity at 1450cm^{-1} band of NH_4^+ and the amount of ammonia adsorbed in six independent experiments for H - 13X Zeolites (exchange degree 97.5%) at 320 K.

The amounts of ammonia reacting with the Brønsted acid sites were calculated from the intensities of the NH_4^+ at 1450cm^{-1} and the extinction coefficient of this band [8].

The amounts of ammonia reacting with Lewis acid sites equal to the subtraction of the amounts of ammonia reacted with Brønsted acid sites from the total amounts of ammonia introduced in the cell. In Figure (8), the integrated intensities of 1450cm^{-1} band was noticed after chemisorbed ammonia with Na-H-13X Zeolites samples of different exchange degrees, an increase of Na/H exchange degree resulted in an increase of the intensity of the Si-OH-Al band.

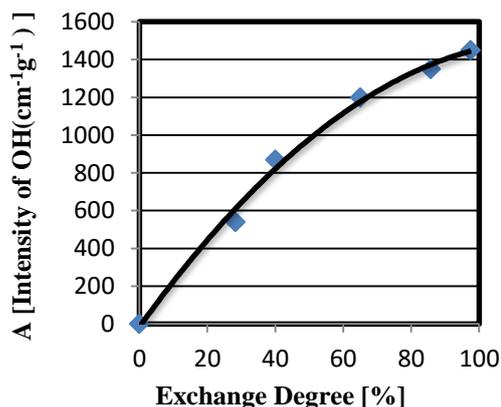


Figure (8): The integrated intensities of the of OH groups after ammonia adsorption in Na-H-13X Zeolites at different exchange degrees

3.2. The concentration of OH in Na-H-X Zeolites

Figures (2), (3), (4), (5) and (6) presents the spectra of OH groups in Na-H-13X Zeolites measured by Fourier transformation infrared spectroscopy (FTIR) for the samples with

different exchange degrees and after adsorption of ammonia. In Na-H-13X zeolites the presence of strong Brønsted acid sites is confirmed by IR bands in the region of frequency 3464-3441 cm^{-1} .

Many factors influence the position of this band.

Increasing the exchange degree resulted in an increase of the intensities of the Si-OH-Al band, and resulted in a shift of the band from 3464 to 3441 cm^{-1} . The intensity of OH band depends on the concentration of OH as well as the extinction coefficient of OH band [15].

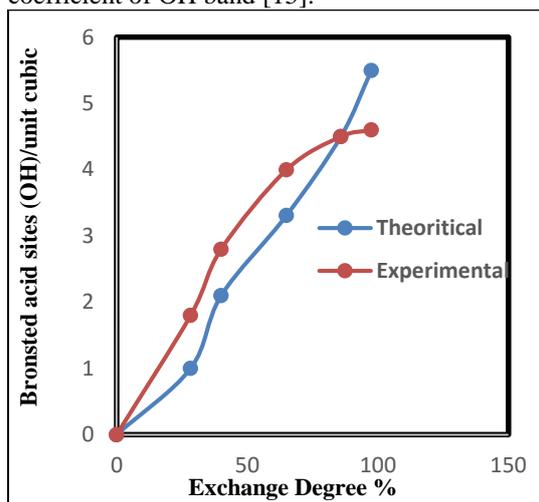


Figure (9): (a) The concentration of OH groups in Na-H-X Zeolites as a function of exchange degree (b) The theoretical amount of hydroxyls (amount of Al minus amount of Na)

The concentration of acidic hydroxyls in HX Zeolites was determined (in IR experiments of ammonia adsorption). The spectrum of chemisorbed ammonia showed practically only the bands of ammonia ions (at 1450 cm^{-1}).

In Figures (2), (3), (4), (5) and (6) appeared one band at 1636 cm^{-1} which resulted from reaction of ammonia with Lewis acid sites. This band at 1636 cm^{-1} is very weak, that means very low concentration of Lewis acid sites in our Na-H-13X Zeolites samples and that is agree with the results in [5, 6, and 7]. Figure (9) presents the theoretical and experimental values of concentration of protonic sites (Si-OH-Al) for each exchange degree (the amounts of Brønsted acid sites / unit cube) in Na- H-13X-Zeolites, experimental values calculated practically from the experiments of ammonia sorption, which is not very different from the values calculated theoretically from the composition of the zeolites, the theoretical values of the concentration of protonic sites calculated from (the amounts of Al minus the amounts of Na) [8].

The effect of exchange degrees on the acid strength of hydroxyls in Na-H-13X Zeolites was obtained after ammonia adsorption and found the relation between the stretching frequencies of OH

groups in NaH-X and the exchange degrees. In Figure (10) notice the stretching frequencies of OH groups decreases with increasing the exchange degrees. The data obtained from Figure (10) give evidence that acid strength increased with increasing the exchange degrees, the information on the acid strength in Na-H-13X Zeolites was obtained by comparing the values of stretching frequencies and extinction coefficient of OH [15]. Meloni et. al. studied the characterization of the acidity by both calorimetry and IR and concluded that acid strength increased with the Si/ Al ratio [16].

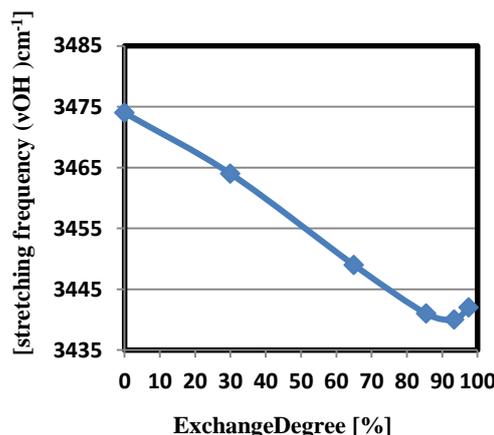


Figure (10) The stretching frequency of OH groups (vOH) cm^{-1} in Na-H-13X Zeolites as a function of Na/ H exchange degrees.

3.3. Homogeneity of the OH groups in NaH-13X Zeolites

Figure (2) shows one distinct Si-OH-Al band at 3464 cm^{-1} , that means OH groups in NaH-13X zeolites are homogeneous and have the same geometry of all $(\text{AlO})_3\text{SiOHAl}(\text{OSi})_3$ groups.

The spectra of OH groups in NaH-13X zeolites of different exchange degrees are presented in Figures (2), (3), (4), (5) and (6), notice the intensity of the Si-OH-Al band increase with increasing the exchange degree and also a shift of the band from 3464 to 3441 cm^{-1} . Heterogeneity of OH groups in HZSM-5, Na-HX, H-Mordenite were studied by Datka, Gil [7]. They found that all the OH groups were first neutralized by ammonia adsorption at 320K, ammonia was subsequently desorbed at vacuum by stepwise heating at increasing temperatures (480-730K) IR spectra were recorded at 320K upon each desorption step. They concluded that if OH groups are heterogeneous, then the less acidic OH of the highest stretching frequency would have released ammonia at lower desorption temperature than the more acidic OH of lower stretching frequency. Therefore, the IR bands of OH groups that are restored at ammonia desorption shifts to lower frequency with the increase in desorption temperature. They found in

H-Mordenite the heterogeneous band of restoring OH is shifted by 9 cm^{-1} , but in the case of homogeneous OH groups in NaHX the shift in frequency was only 2 cm^{-1} [7]. The results of these experiments of ammonia sorption and desorption agree well with our conclusion that Si-OH-Al groups in Na-H-13X Zeolite are homogeneous.

4- Conclusions

1-Effect of delamination on the acid properties of Na-H-13X-faujasites was studied and from the values of intensity of OH, the extinction coefficients and frequency shifts $\Delta\nu=23\text{ cm}^{-1}$ of the IR spectra after ammonia adsorption are concluded that the acidity increased with increasing dealumination that agrees with the results of catalytic studies [8].

2- The intensity of OH band depends on the concentration of hydroxyls as well as on the extinction coefficient of OH band.

3-Increasing the exchange degree results in an increase in the concentration of the protonic sites measured by NH_3 sorption.

4- Our conclusion on the homogeneity of OH groups in NaH13X agrees with the results of Datka et al [17], [18].

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الخلاصة

تم استخدام طريقة مطيافية الأشعة تحت الحمراء لقياس و لتمييز تراكيز المواقع الحامضية نوع برونستد و المواقع نوع لويس في الحفاز من نوع NaH-13X Zeolites . تم الحصول على النماذج من الحفاز بالتراكيز وزنا (28,40,65,85.8,97.5%) باستخدام طريقة التبادل الأيوني ثم اتبعت بطريقة ازالة الألمنيوم. تم الاستنتاج بان مجموعة الهيدروكسيل منتظمة الحامضية وذلك بتحليل اطياف الأشعة تحت الحمراء للمواقع الحامضية (مجموعة الهيدروكسيل OH) بعد الامتزاز للامونيا. تم الاستنتاج بوجود مواقع حامضية متنوعة في الحدود للمطياف ($3,800-3,000 \text{ cm}^{-1}$) لمجموعة الهيدروكسيل (OH) مثل وجود مواقع حامضية قوية من نوع برونستد تقريبا عند 3441 cm^{-1} , واخرى اقل حامضية تقريبا عند 3464 cm^{-1} , واخرى ضعيفة وقليلة من نوع لويس عند 1636 cm^{-1} . من الممكن الاستنتاج بان تركيز مجموعة الهيدروكسيل (OH) يزداد بازدياد نسبة التبادل الأيوني وبزيادة نسبة ازالة الألمنيوم . تم حساب تركيز المواقع الحامضية في النماذج وذلك من معامل الاندثار وازاحة التردد الموجي في المطياف بسبب ارتباط الهيدروجين في الهيدروكسيل مع الامونيا. كان الانحياز للتردد الموجي للهيدروكسيل للنموذج ذو تركيز 97.5% . ($\Delta\nu_{\text{OH}} = 23 \text{ cm}^{-1}$). ان معرفة مقدار ونوع حامضية الحفاز مهم بالذات في التفاعلات التي تتطلب وسطا حامضيا