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Structural and Ammonia Adsorption Properties of the Gördes Clinoptilolite After HCl Acid Treatment

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Highlights

- NH_3 uptake was investigated at 298 K using a volumetric device.
- Characterization of samples were investigated by XRD, XRF, SEM and N_2 adsorption.
- CLN had the highest ammonia uptake (5.01 mmol.g^{-1}).

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Abstract

The effect of activation with HCl on the ammonia adsorption characteristics of natural Gördes clinoptilolite was studied in order to evaluate the usability of this mineral in various environments where ammonia removal is required, such as livestock facilities. Clinoptilolite was treated with HCl solutions (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 M) at 90°C for 4 h. XRD, XRF, FT-IR, TGA, DTA and N_2 adsorption techniques were used for structural and thermal characterization of the adsorbents. NH_3 adsorption isotherms were measured volumetric analysis at 298 K up to 100 kPa. Acid activation not only caused textural and structural changes such as removal of exchangeable cations but also affected the thermal behavior and gas retention of the clinoptilolite. Nitrogen adsorption results showed that it is possible to improve the specific surface area and micropore area values of clinoptilolite with acid activation up to 1.5 M. In addition, the NH_3 adsorption capacities of clinoptilolite samples (4.33-5.01 mmol.g^{-1}) were compared with the ammonia removal data of natural and synthetic zeolites (1.77 - 9.32 mmol.g^{-1}) reported in previous studies.

1. INTRODUCTION

The agricultural and livestock sector is one of the most indispensable parts of society in the 21st century. Thanks to them, billions of us can find food in our local supermarkets. But as with all technological conveniences, we pay the price for this convenience in the form of air pollution. The quality of the air indoors and outdoors is becoming more and more important [1]. Many studies have shown that indoor volatile compounds can cause medical problems such as irritation of mucous membranes [2]. Ammonia, a colorless, malodorous and dangerous gas, is one of the air pollutants [3-5]. It consists of one nitrogen and three hydrogen atoms. Ammonia has a molar mass of 17.0312 g/mol and a Debye dipole moment of 1.5 due to its asymmetric shape [5]. The concentration of ammonia in pig farms can affect the growth and health of the animals. For example, an inflammatory response has been observed in the respiratory system of pigs exposed to ammonia concentrations of 100 and 150 ppm [6]. Furthermore, 100-400ppm ammonia causes eye and throat irritation in humans [7]. Respiratory symptoms are reversible. However, chronic bronchitis has been reported in some cases [8]. Livestock and agricultural activities also cause more ammonia emissions than fuel combustion, vehicles and all industrial activities [9]. Sensitive crops and human health are directly affected by atmospheric concentrations of ammonia [10]. Therefore, ammonia emissions from livestock farms and agricultural land need to be controlled and zeolites may be good candidates for these applications.

Zeolites are alumina-silicate minerals that have been known for almost three centuries [11]. Their crystalline framework is based on simple tetrahedral blocks (TBs) with the general formula TO_4. Here O refers to oxygen and T can be silicon or aluminum. TBs combine to form three-dimensional networks

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*Corresponding author, e-mail: burcuerdogan@eskisehir.edu.tr containing cavities, channels, exchangeable framework cations and water [12]. In addition, the different ways in which these TBs can be linked give rise to more than fifty types of natural zeolites found in nature [11-13]. Clinoptilolite is a member of the heulandite (HEU) group. The general formula of clinoptilolite can be given as $(Na,K)_6(Al_6Si_{30}O_{72}).20H_2O$. Unit cell parameters are a=17.62 Å, b=17.91 Å, c=7.39 Å and β = 116°16'. Its framework structure with monoclinic C2/m symmetry is almost identical to that of heulandite [13]. However, clinoptilolite has greater structural stability than heulandite at high temperatures. Therefore, Mumpton defines clinoptilolite as a zeolite that survives overnight heating at 450 °C [14]. Clinoptilolite has a 2D channel system consisting of three channels. Channels A and B lie along the c-axis and channel C intersects these channels along the a-axis. Thus, the structure has no channel along the b-axis, matter transfer in clinoptilolite occurs only along the a- and c-axes. Channel A is the largest tunnel with a 10-membered ring in the clinoptilolite structure. Channels B and C consist of 8-membered rings and are relatively smaller than channel A [11,13]. Clinoptilolite has four cation sites in these channels, named M(1), M(2), M(3) and M(4) (Figure 1). M(1) site is channel A. Normally Na^+ and Ca^{2+} cations are found at this site. M(4) is in the center of channel A and contains the Mg^{2+} cation coordinated with H_2O molecules. The M(2) site is located in channel B and is usually occupied by Ca^{2+}, and finally, the M(3) region is in the center of the C channel and there are K^+ ions in this region. Besides these well-known sites, there are studies showing that clinoptilolite can have other cation positions containing Cs^+, Ag^+, Pb^{2+}, Cd^{2+}, Hg^{2+} ions [15-18]. Clinoptilolite can be used for gas separation and removal of toxic gases due to its structural advantages [19-24].

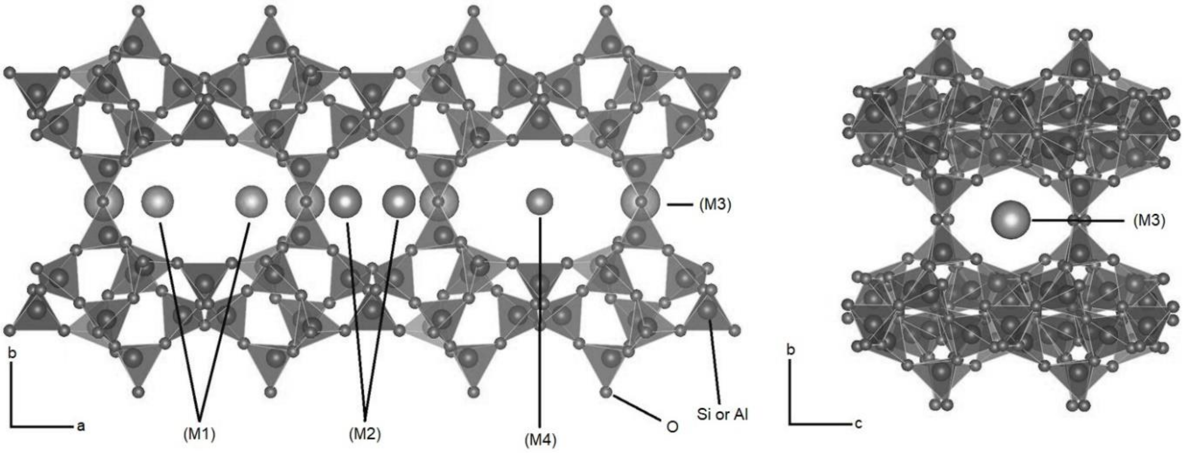

Figure 1. *View of clinoptilolite framework and cation sites along c-axis (a) and a-axis (b)*

Prior to gas adsorption applications, it may be necessary to modify and optimize the structure of the clinoptilolite. Therefore, applications such as cation exchange and acid activation are common [18,25]. Acid activation increases the BET surface area [26] and the number of acid sites of clinoptilolite [27] and opens blocked channels [28] by dealumination and replacement of H^+ ions with exchangeable cations. On the other hand, increasing acid concentrations can cause the crystal structure of clinoptilolite to collapse [29]. A number of studies have been conducted which investigate the adsorption of ammonia on natural and synthetic zeolites [3,4,30-37]. However, the effect of activating clinoptilolite with different concentrations of HCl solutions on ammonia adsorption applications has not been investigated. This study was conducted with the objective of examining the impact of acid activation on ammonia removal by clinoptilolite in environments such as the poultry and cattle industry.

2. MATERIAL METHOD

2.1. Materials and Chemicals

Clinoptilolite (CLN) from Gördes was used in <63 μm fractions. The clinoptilolite samples were then stirred in deionized water at 50°C for 4 h to eliminate soluble impurities from the structure. Acid-treated forms of clinoptilolite were prepared to compare the physicochemical and gas adsorption characteristics. First, five grams of clinoptilolite were treated with HCl solutions (0.5-3.0 M) at 90 °C for 4 h. The solution mixtures containing clinoptilolite were then filtered, washed repeatedly with deionised water at boiling temperature and dried at 110 °C for 24 h. The resulting samples were labelled CLN-HX, where X indicates the acid molarity. HCl was supplied by Merck.

2.2. Experimental

A chemical analysis was conducted on powdered samples fused with lithium tetraborate using X-ray fluorescence spectroscopy (Rigaku ZSX Primus instrument). Loss of Ignition (LOI) was quantified by mass measurement following the samples' heating to 1000°C at a rate of 10°C per minute, a period of one hour, and subsequent cooling to room temperature at the same rate. Powder XRD patterns of the samples were collected using Bruker D8 Advance device operating with CuK_α (λ = 1.5406 Å) in the range of 2θ values 5-40° and step range of 0.02°. DTA and TG analyses were carried out on a Setaram Setsys Evolution equipment from 30 to 1000 °C at a heating rate of 10 °C min^{-1}. For TG-DTA analyses, approximately 35 mg of the sample was employed as the carrier gas was N_2. The conventional KBr pellet technique was used for FT-IR analysis. First of all, the samples and KBr were kept in an oven at 100 °C for 3 h. Then, 0.5 mg sample was added into 200 mg KBr and mixed in agate mortar until it became homogeneous. The KBr-sample mix was then pressed with a desktop size manual hydraulic press under a load of 2 Tons for approximately 2 min The clinoptilolite samples for which ammonia adsorption measurements were completed were directly mixed with KBr and pressed under the same conditions. FT-IR spectra were obtained using a BRUKER Vertex 80v spectrometer at 4 cm^{-1} resolution, with 16 scan times in the 400-4000 cm^{-1} wavelength range. All spectral data were collected with an RT-DLaTGS detector at room temperature. The adsorption and desorption of nitrogen (N_2) were evaluated via a Micromeritics 3FLEX analyzer at 77 K. The specific surface areas (S^{BET}) were determined by BET equation ($0.05 < P/P_0 < 0.35$). Micropore surface areas ($S^{\mu P}$) and volumes ($V^{\mu P}$) were determined using the t-plot method. NH_3 isotherms were measured at 298 K up to 100 kPa using Micromeritics 3Flex instrument. Prior to the N_2 and NH_3 adsorption experiments, the clinoptilolites were outgassed at 300 °C for 10 h.

3. THE RESEARCH FINDINGS AND DISCUSSION

3.1. Elemental Analysis

The elemental analysis of the clinoptilolites are given in Table 1. The CLN sample is characterized by high K_2O and CaO and low Na_2O and MgO. Even activation with 0.5 M acid was found to be sufficient for significant dealumination and the replacement of H^+ ions by exchangeable cations (Na^+, K^+, Ca^{2+} and Mg^{2+}). However, a complete dealumination could not be achieved at the acid concentrations used. Owing to the acid treatment, the extra-framework cations and framework Al^{3+} were progressively removed and free amorphous silica, insoluble in the acid solution, was obtained. The SiO_2/Al_2O_3 ratio increased from 5.64 for CLN to 11.66 for the 3.0 M HCl treated sample. The K^+ and Ca^{2+} remaining in the acid treated forms would correspond to the illite and feldspar remaining in the material as shown by the XRD patterns (Figure 2). Previous studies also found a similar effect of acid activation on the elemental composition of clinoptilolite [26,38,39].

3.2. X-ray Diffraction

The powder XRD patterns of the clinoptilolite samples (raw, CLN-H0.5, CLN-H1.0, CLN-H1.5, CLN-H2.0, CLN-H2.5, CLN-H3.0) forms are shown in Figure 2. According to the results, the main clinoptilolite reflections were observed at 2θ= 9.91°, 19.15°, 22.51°, 28.20°, 30.22° with corresponding distances of 8.91 Å, 4.65 Å, 3.95 Å, 3.16 Å and 2.96 Å, respectively [40]. CLN contains 80-85% clinoptilolite as the main mineral. It also contains impurities such as opal-CT (5-6%), illite (2%), feldspar (3%) and amorphous matter (5-10%) according to the method of Esenli and Sirkecioğlu, 2005 [41]. Increasing acid molarity caused a gradual decrease in the intensity of the clinoptilolite peaks and the formation of a broad baseline between 19 and 30° of 2θ. These are indicative of the partial collapse of the structure and the formation of an amorphous phase. Similar broad backgrounds due to acid activation have been reported in previous studies [39]. However, illite and feldspar peaks are still present in the sample activated with 3.0 M HCl solution, indicating that the illite and feldspar are more resistant to acid attack than the clinoptilolite.

Table 1. *Chemical analyses in oxides (%) for the clinoptilolite samples*

Sample	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	LOI
CLN	70.5	12.5	1.17	0.468	5.08	2.20	0.573	7.42
CLN-H0.5	80.0	8.77	1.13	-	2.97	0.467	0.399	6.28
CLN-H1.0	81.4	8.14	1.09	-	2.20	0.460	0.350	6.19
CLN-H1.5	81.3	7.64	1.08	-	1.78	0.411	0.380	7.25
CLN-H2.0	82.1	7.73	0.987	-	1.64	0.410	0.410	6.30
CLN-H2.5	82.4	7.28	0.931	-	1.50	0.418	0.372	6.69
CLN-H3.0	82.6	7.08	0.974	-	1.43	0.399	0.332	6.95

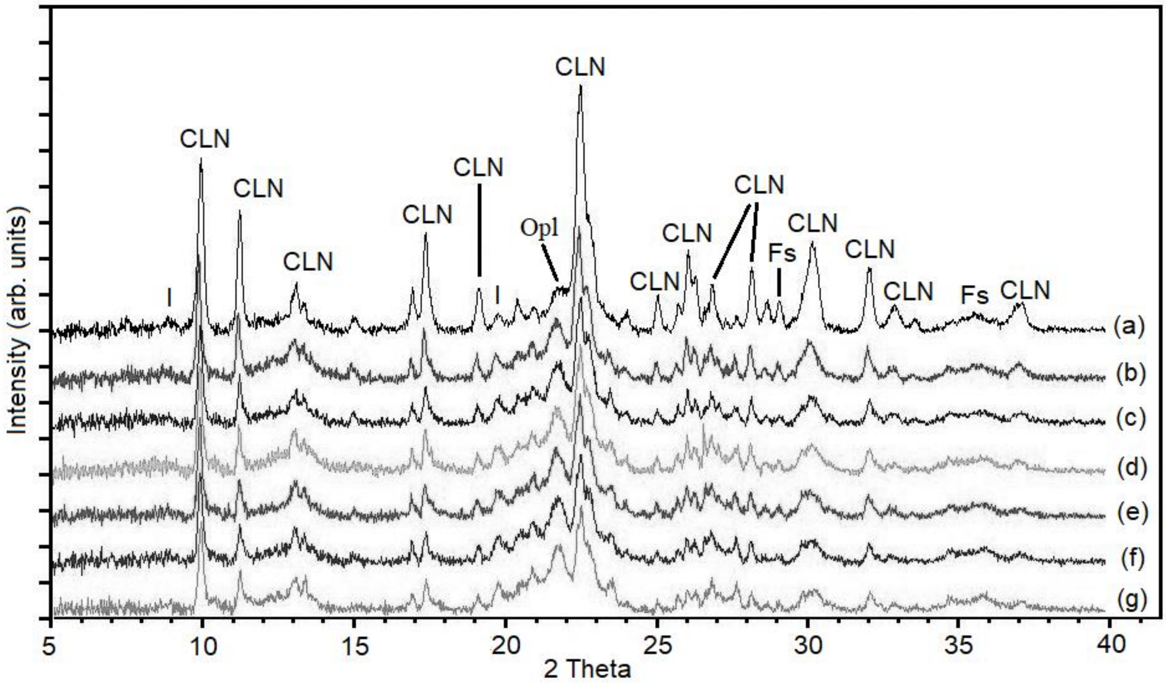

Figure 2. *XRD patterns of CLN (a), CLN-H0.5 (b), CLN-H1.0 (c), CLN-H1.5 (d), CLN-H2.0 (e), CLN-H2.5 (f) and CLN-H3.0 (g) (CLN: clinoptilolite, Opl: opal, Fs: feldspar, I: illite)*

3.3. Thermal Properties

The DTA and TG curves obtained for the clinoptilolites are shown in Figure 3. Strong endothermic peaks at 68 °C and 153 °C on the DTA curve of CLN with the largest mass loss of 2.48% between 30 and 200 °C are owing to dehydration of the loss of water located in the voids and bound to the extra-framework cations. For temperatures between 200 and 600 °C, the mass loss is 4.34%. Between 600 and 800 °C, the remainder of the strongly associated water is gradually eliminated with a mass loss of 0.49% due to dehydroxylation. As seen from Figure 3, the clinoptilolite samples presented the continuous mass loss curves. It was found that the thermal properties of clinoptilolite samples varied in terms of both the SiO_2/Al_2O_3 ratio and the extra-framework cation composition. The mass losses for the acid activated clinoptilolites (7.19 - 7.41%) were lower than those for the CLN (7.45%). In addition, the intensity of the first two endothermic peaks gradually decreased in the acid modified forms. These results may be related to the dealumination and the elimination of the non-framework cations (Table 1).

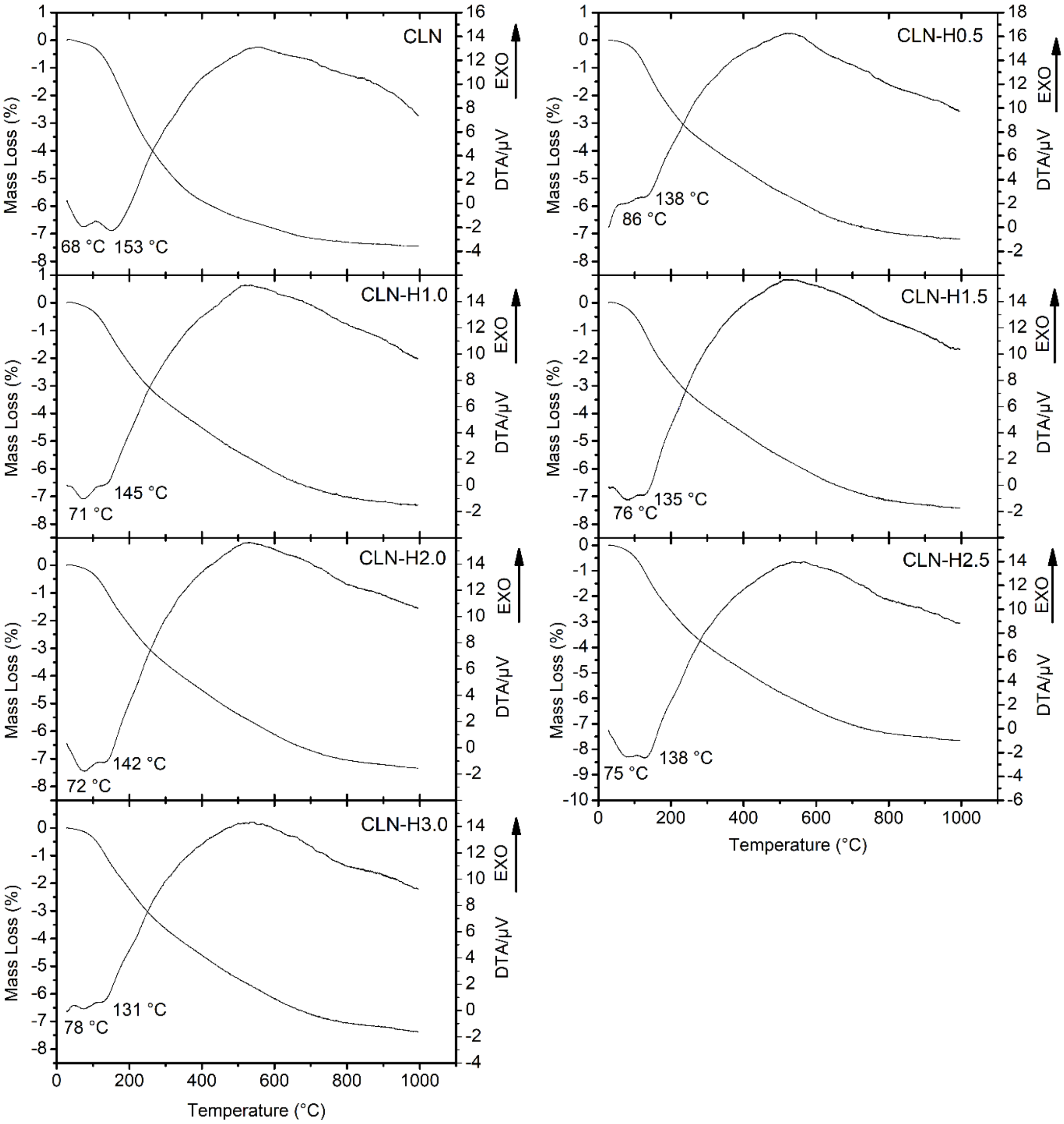

Figure 3. *TG/DTA curves of the raw and acid-activated clinoptilolites*

As the majority of the water in the structural cavities is bound to non-framework cations, the dehydration of natural zeolites is contingent upon the presence of additional framework cations, with particular emphasis placed on their hydration energy. Natural clinoptilolites containing cations with high hydration energies contain significantly more water and retain this water up to higher temperatures.

3.4. FT-IR

Figure 4 presents the FT-IR spectra of all clinoptilolites. The characteristic vibrations of the clinoptilolite structure can be seen between 400-1200 cm^{-1}. The 420-500 cm^{-1} vibrations are associated with internal tetrahedral T-O bending mode. The 605 cm^{-1} band is the result of external tetrahedral double ring vibrations. The strongest band at 1050 cm^{-1} belongs to the external tetrahedral linkage asymmetric stretching mode [42,43]. After acid treatment, the band at 1051 cm^{-1} shifted to a higher frequency at 1084 cm^{-1} owing to dealumination and partial breakdown of the clinoptilolite framework [38,44]. Partial structural breakdown and dealumination can also be observed from the relative changes in bands around 467 and 605 cm^{-1}. The intensity of the clinoptilolite fingerprint band at 605 cm^{-1}, which represents the amount of clinoptilolite in the tuff, decreases with acid treatment, while the characteristic amorphous silica band at 460 cm^{-1} and 795 cm^{-1} increases. This indicates the formation of amorphous silica, which is also seen in the XRD data (Figure 2) [39]. The band at 1638 cm^{-1} is related to O-H bending vibrations of water [45]. The vibrational bands around 3434 and 3630 cm^{-1} reflect the Si-OH groups and bridging hydroxyls (Si-O(H)-Al), respectively [46]. After ammonia adsorption, the FT-IR spectrum of the clinoptilolite structure remains almost the same, but a band appears at around 1400 cm^{-1}. Ammonium formation is a known phenomenon in ammonia-zeolite interactions [47-49]. This band can therefore be attributed to the ν4 stretching vibrational mode of the ammonium ion [50,51].

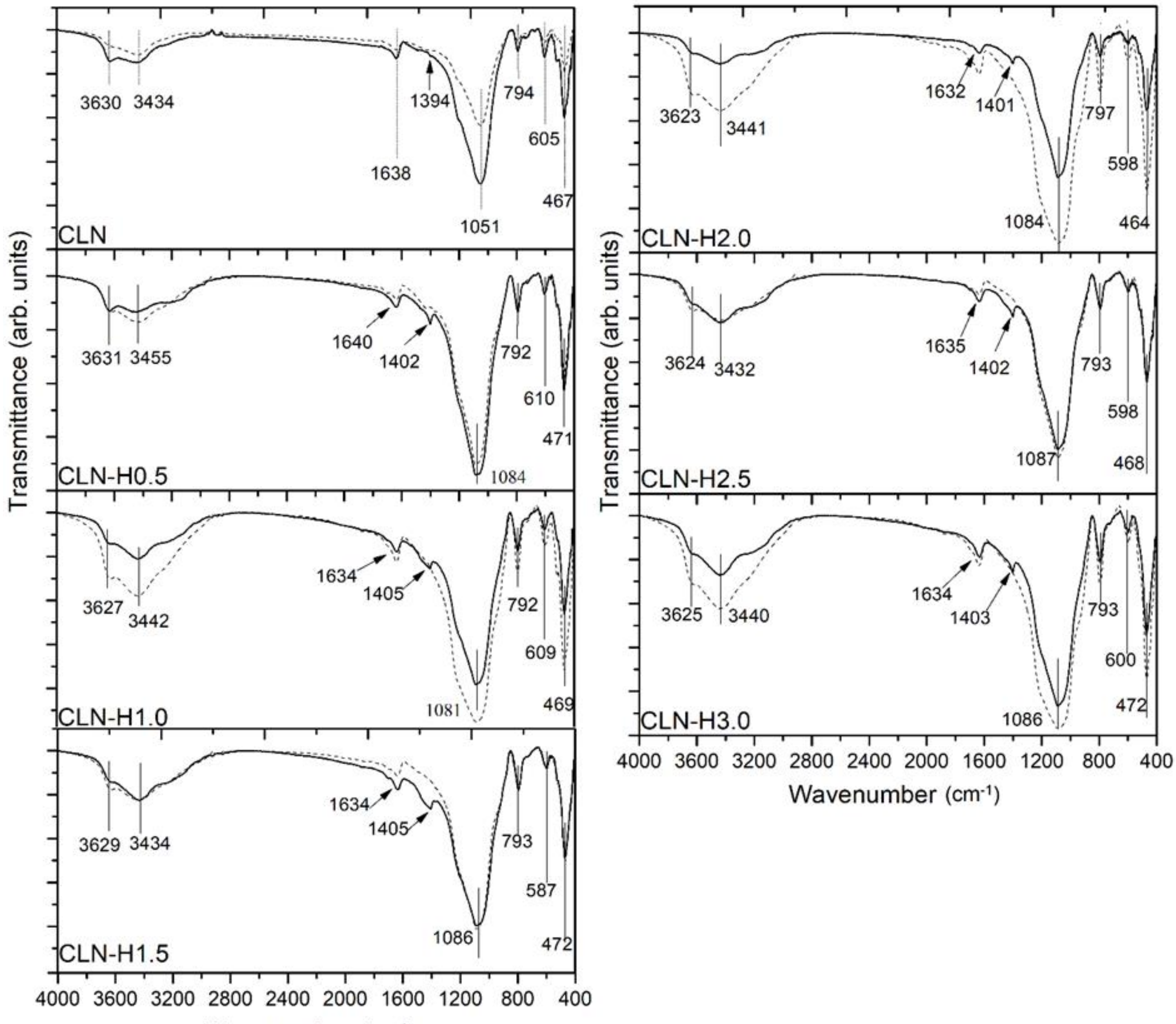

Figure 4. *FT-IR spectra of the raw and acid-activated clinoptilolites before (dashed line) and after (solid line) the ammonia adsorption*

3.5. N_2 Adsorption

N_2 adsorption-desorption isotherms for all the clinoptilolite samples are given in Figure 5 and their textural characteristics are tabulated in Table 2. All isotherms are of type IV and have a hysteresis loop associated with pore condensation [52]. As seen from the shape of the isotherms, the clinoptilolite sample contains micropores (pore width < 2 nm) in addition to mesopores (pore width in the range 2-50 nm). The initial part of the isotherms can be attributed to monolayer-multilayer adsorption [52]. The specific surface area of the sample increased from 42 m^2.g^{-1} for CLN to 178 m^2.g^{-1} for CLN-H1.5.

This increase in the BET surface area is owing to partial loss of extra-framework cations, dissolution of aluminum, elimination of pore-blocking impurities and formation of secondary porosity due to dissolution of free bonds. Both the BET surface area and microporous surface area values decreased in activated samples with acid molarity greater than 1.5 M. The CLN-H3.0 sample had the lowest specific surface area (163 $m^2.g^{-1}$) and microporous surface area (113.97 $m^2. g^{-1}$) among the acid modified forms.

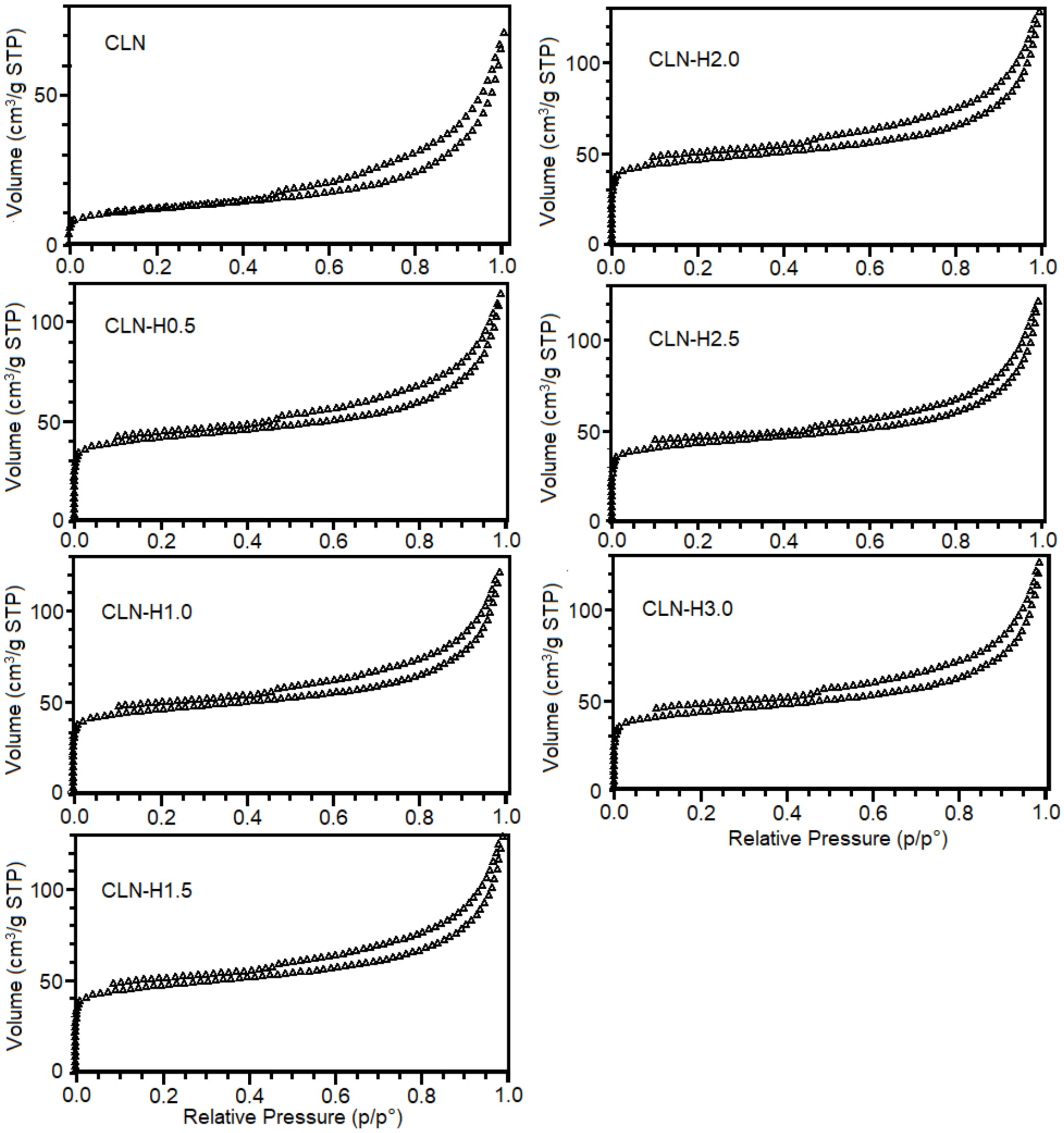

Figure 5. *Nitrogen adsorption isotherms of raw and acid activated clinoptilolite*

Table 2. *N_2 data of the raw and acid activated clinoptilolites*

Sample	S^{BET} ($m^2.g^{-1}$)	$S^{\mu P}$ ($m^2.g^{-1}$)	$V^{\mu P}$ ($x10^{-2}$ $cm^3.g^{-1}$)
CLN	42	11.99	0.49
CLN-H0.5	157	112.18	4.58
CLN-H1.0	173	127.50	5.18
CLN-H1.5	178	129.35	5.30

CLN-H2.0	175	125.97	5.15
CLN-H2.5	165	122.30	4.91
CLN-H3.0	163	113.97	4.66

This result for CLN-H3.0 sample, where the acid was used at the highest molarity, can be attributed to the fact that delamination and partial destruction of the clinoptilolite crystal structure occurs at the highest rate due to acid activation compared to other acid modified forms. This finding is consistent with the XRF results (Table 1), XRD (Figure 2.) and FT-IR (Figure 4.) analyses.

3.6. NH_3 Adsorption

Ammonia adsorption isotherms and absolute uptake for clinoptilolite samples at 298 K to 100 kPa are given in Figures 6 and 7 and Table 3. According to the classification given by IUPAC, the isotherms are of type I. NH_3 isotherms are generally observed on microporous materials like activated carbons, certain porous oxides and zeolites [52]. At relatively low pressures, high adsorption amounts are observed due to the high adsorption potential and narrow pore diameter. However, at relatively high pressures, the adsorption value approaches a constant. This indicates that the accessible micropore volume exerts a more pronounced influence on the adsorption process than the internal surface area [52,53].

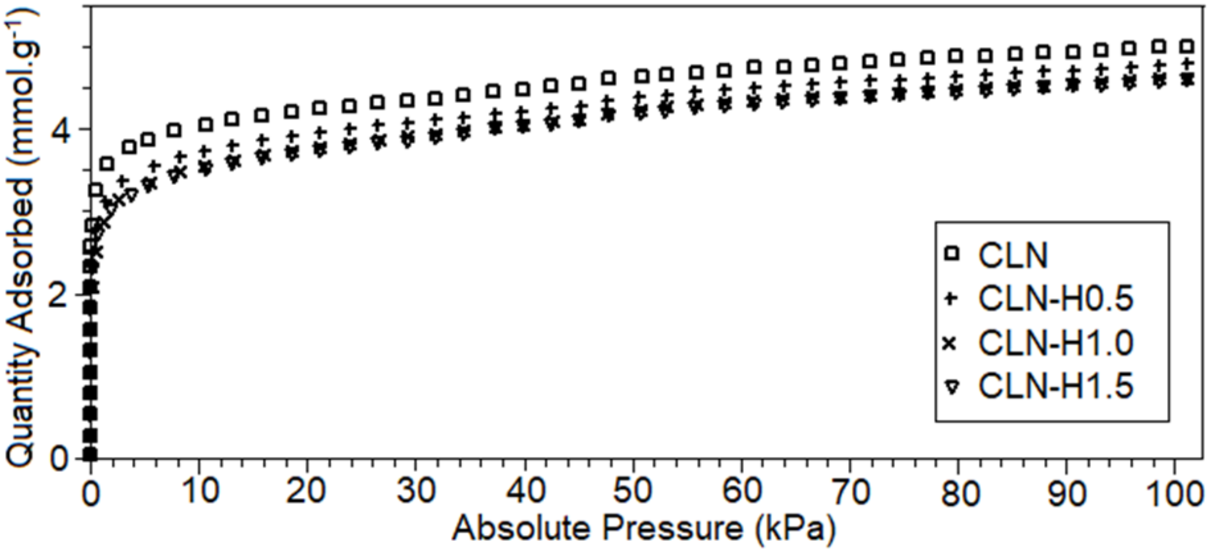

Figure 6. *NH_3 adsorption isotherms of CLN, CLN-H0.5, CLN-H1.0 and CLN-H1.5 samples*

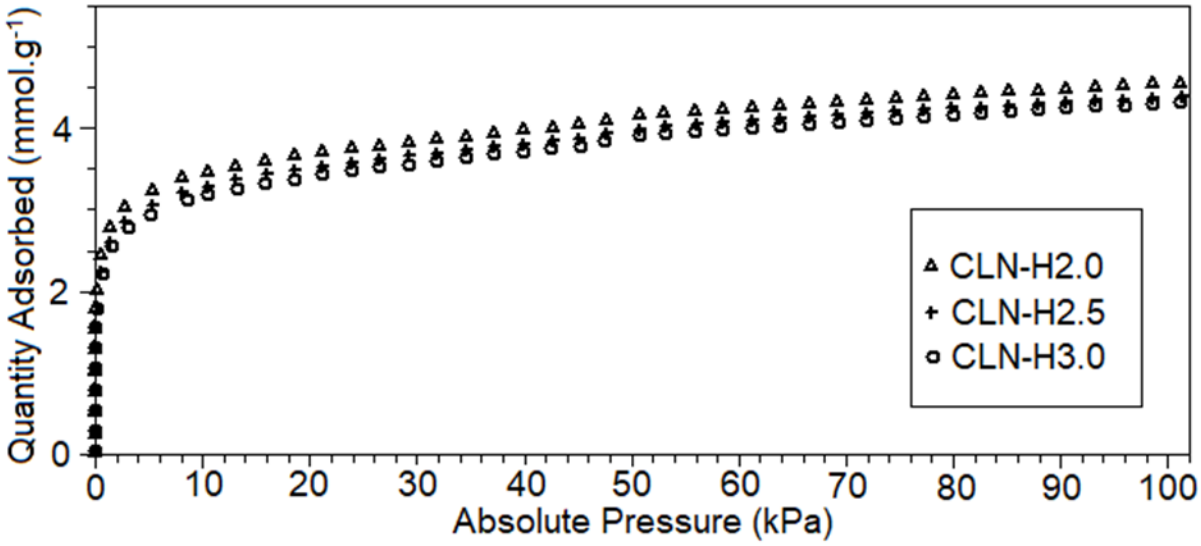

Figure 7. *NH_3 adsorption isotherms of CLN-H2.0, CLN-H2.5 and CLN-H3.0 samples*

The NH_3 molecule has a kinetic diameter of 0.26 nm can easily diffuse through the pores of clinoptilolite. In this study, the ammonia uptake decreased in the order CLI > CLI-H0.5 > CLI-H1.0 > CLI-H1.5 > CLI-H2.0 > CLI-H2.5 > CLI-H3.0 (Figures 6 and 7). The maximum uptake of ammonia is exhibited by CLN (5.01 $mmol.g^{-1}$) and the minimum by CLN-H3.0 (4.33 $mmol.g^{-1}$). Although all acid-treated forms have higher surface area values (157-178 m2.g^{-1}) than the raw sample CLN (42 $m^2.g^{-1}$), the adsorption capacities of these samples are lower (4.33-4.79 $mmol.g^{-1}$) than that of raw CLN (5.01 $mmol.g^{-1}$), because of the removal of exchangeable cations and the consequent reduction in the local electric field. In addition to changes in structure due to acid modification and dealumination, this clearly demonstrates the effect of removal of extra framework cations on ammonia adsorption. As ammonia is a highly polar molecule, it tends to share a lone pair of electrons with these exchangeable cations. At high pressures, however, the number of polar molecules adsorbed is directly related to the cation density in the framework [54]. In acid-treated samples, the ammonia uptake decreased with increasing acid molarity. The variation in ammonia gas adsorption capacity for natural clinoptilolite and its acid-treated forms indicated that the electrostatic and the dispersion forces played the role in the adsorption. Acid modification resulted in the exchange of the exchangeable cations with H^+ cations [55,56]. Due to the dealumination process, the number of permanent negative sites in the clinoptilolite structure decreased and the zeolite surface became less negative [55,57]. The high affinity of sample CLN for NH3 is therefore due to the interactions of the permanent dipole moment (1.47 Debye) of ammonia molecule with the electric field generated by cations in the clinoptilolite. As shown in Table 3, the uptake of ammonia by sample CLN (5.01 $mmol.g^{-1}$) was higher than that of natural (0.63 $mmol.g^{-1}$) and acid-treated clinoptilolite (1.12-1.27 $mmol.g^{-1}$) from the Ninny deposit, Hrabovec [34], dealuminated faujasite from Wessalith DAY F20 (1.77 $mmol.g^{-1}$) [35], clinoptilolite (0.72 $mmol.g^{-1}$) [31], clinoptilolite (1.01 $mmol.g^{-1}$) [32], clinoptilolite (Slovakia) (0.71 $mmol.g^{-1}$) [58] and lower than a clinoptilolite-rich tuff from Thrace, NE Greece (5.28 $mmol.g^{-1}$) [33] and clinoptilolite from Mud Hills CA (5.90 $mmol.g^{-1}$) [35These findings demonstrate that the origin, mineral composition, cationic content, and impurity concentration of natural clinoptilolite have a significant impact on the capacity of this material to retain ammonia because natural clinoptilolite has a different mineralogical and chemical composition depending on the mineral deposit from which it was formed and mined. Furthermore, CLN showed lower ammonia adsorption capacity than 13X zeolite Baylith WE894 (9.32 $mmol.g^{-1}$) [35], 5A Lancaster 5830 (7.81 $mmol.g^{-1}$) [35], 4A Baylith TG242 (8.71 $mmol.g^{-1}$) [35], silica gel 40 Fluka 60736 (6.25 $mmol.g^{-1}$) [35], due to textural and structural differences. Synthetic zeolites generally have a higher gas retention than natural ones owing to their uniform structure, but are more expensive [59]. In addition, the abundance of the clinoptilolite type natural zeolites and their high sorption capacities provide cost effective and environmentally friendly solutions for gas adsorption applications.

Table 3. *Comparison of NH$_3$ adsorption capacities of the present work with literature data at 298 K*

Sample	**Pressure (kPa)**	**NH$_3$ Adsorption Capacity (mmol.g^{-1})**	**Reference**
CLN	101	5.01	Present Study
CLN-H0.5		4.79	
CLN-H1.0		4.62	
CLN-H1.5		4.59	
CLN-H2.0		4.58	
CLN-H2.5		4.39	
CLN-H3.0		4.33	
Clinoptilolite	101	~1.01 (14.155 mg N g^{-1})	[31]
Clinoptilolite	101	~0.72 (10.10 mg N g^{-1})	[32]
Clinoptilolite-rich tuff Pentalofos, Greece	101	~5.28	[33]
Clinoptilolite treated with 1.0 M Mg(NO$_3$)$_2$	101	5.37	[58]
Natural Clinoptilolite from Nizny Hrabovec	101	0.63	[34]
pre-treated with 30 % H$_2$SO$_4$	101	1.27	
pre-treated with 30 % H$_3$PO$_4$	101	1.17	
pre-treated with 30 % HNO$_3$	101	1.12	
Clinoptilolite (USA)	101	5.90	[35]
Faujasite dealuminated	101	1.77	
Pentasil dealuminated	101	2.34	
4A zeolite (Baylith TG242)	101	8.71	
5A zeolite (Lancaster 5830)	101	7.81	
13X zeolite (Baylith WE894)	101	9.32	
Alumina (LaRoche 1597)	101	3.01	
Silica gel 40	101	6.25	
Clinoptilolite (Slovakia)	fixed bed	0.71 / (12.2 mg g^{-1})	[58]

Many studies in the literature have investigated ammonia adsorption on natural and synthetic zeolites [3,4,30-37]. The innovative aspect of this study is to examine the influence of activating Gördes clinoptilolite with different concentrations of HCl solution on ammonia adsorption applications. As a result, Raw CLN, which has the highest ammonia adsorption capacity among the samples used in this study, was found to be a suitable material for ammonia gas removal.

4. CONCLUSIONS

In this study, Gördes clinoptilolite was investigated to determine the influence of HCl activation on its physicochemical and ammonia adsorption characteristics. Due to the dealumination and partial dissolution of the crystal structure, with increasing acid concentration the peak intensities of clinoptilolite decreased. As a result of the treatment with HCl acid, it was determined that there were notable alterations in the elemental composition of the clinoptilolite and in the SiO_2/Al_2O_3 ratio (from 5.64 to 11.66). The transmittance at 605 cm^{-1}, the characteristic band related to clinoptilolite content, decreased with increasing acid concentration. Acid activation up to 1.5 M improved both microporosity and specific surface areas, but acid treatment with HCl did not increase the ammonia uptake of Gördes clinoptilolite. The decrease in gas adsorption capacity of the acid-treated clinoptilolites indicated the effect of the removal of exchangeable cations on NH_3 affinity. Therefore, The results indicated that the ammonia uptake of the samples is dependent on the type and number of cations present in the channels, rather than the BET surface area. The higher ammonia uptake of CLN (5.01 $mmol.g^{-1}$), a raw sample from the Gördes region, compared to acid-treated forms (4.33-4.79 $mmol.g^{-1}$) can be recommended for ammonia removal in poultry houses and livestock industries without additional HCl acid treatment.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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