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The Nature and Catalytic Activity of Hydroxyl Groups in Clinoptilolite

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IR spectroscopy of NH_4-clinoptilolite after deammoniation at 400°C shows a single hydroxyl band at 3620 cm^{-1}, slightly asymmetric to the lower wave numbers. The deammoniation is reversible and stoichiometric: for each NH_4^+ ion that decomposes an acidic hydroxyl group is formed in the lattice. At temperatures higher than 400°C dehydroxylation occurs: two lattice hydroxyls condense, water is evacuated, and Lewis acid sites are created. Comparison of the adsorption of NH_3 and pyridine on the H-clinoptilolite, shows that about 10% of the lattice hydroxyl groups are on the external surface. The catalyst is active for the isomerization of 1-butene. The isomerization activity changes with the amount of hydroxyl groups on the external surface. Lewis acid sites are created at elevated temperatures, but have no secondary influence on the catalytically active Brønsted sites.

INTRODUCTION

Although a great number of publications have appeared during the last decade dealing with synthesis, structure, and catalytic properties of zeolites, several types of zeolites are only rarely examined. One of these zeolites is clinoptilolite. The structure of this mineral and its relationship with heulandite was subject to several contradictory explanations. Schaller (*1*) first described this type of zeolite in 1932. Mumpton (*2*) reported a comprehensive review concerning the occurrence, origin, and properties of clinoptilolite. He concluded that heulandite and clinoptilolite have the same aluminosilicate framework, but that the two minerals are different as to their origin, cation content, and especially to their thermal stability. Indeed, heulandite transforms into heulandite B at about 230°C and becomes amorphous at 350°C. Clinoptilolite remains stable up to about 700°C.

Following Breger *et al.* (*3*) the chemical composition of natural clinoptilolite is $X_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 3H_2O$, X being predominantly K and Na, and only to a minor extent Ca and Mg. The chemical composition of heulandite is $CaO \cdot Al_2O_3 \cdot (6 \text{ or } 7)SiO_2 \cdot 2H_2O$. Most of the authors attribute the difference in thermal stability to this difference in Si:Al ratio. Merkle and Slaughter (*4a*) determined the structure of heulandite, being the *iso*-structural form of clinoptilolite. A stereoscopic drawing of the heulandite structure was published recently (*4b*). Clinoptilolite is monoclinic (C_m) and consists of aluminosilicate layers formed by 6-, 5-, and 4-membered rings of tetrahedra. The layers are in the *ac* plane and are cross-linked together by oxygen bridges. In this way, four kinds of channels are formed parallel to the *ac* plane in three different directions. Two kinds of channels are parallel to the *c* axis and consist of 10- and 8-membered rings with internal dimensions of 7.05 × 4.25 Å and 4.60 × 3.95 Å, respectively. The third kind of channels is parallel to the *a*-axis and consist of 8-membered rings with dimensions of 5.40 × 3.90 Å. The fourth kind of channels are formed by 8-

membered rings of tetrahedra (5.20 × 3.90 Å) and form an angle of about 50° with the *a* direction.

Barrer, Papadopulos, and Rees (*5*) investigated the exchange of sodium ions for alkylammonium ions in clinoptilolite. They could give a good interpretation of their results based on the structural parameters given by Merkle and Slaughter (*4a*). The ion exchange properties were investigated also for inorganic cations (*6*, *7*). In both cases it was concluded that clinoptilolite has a double ion sieve ability, corresponding to the two kinds of channels with different dimensions.

The H-form of clinoptilolite can be obtained after heat treatment of the NH_4^+-form or acid treatment of the natural mineral (*12*, *13*). H-clinoptilolite shows significant catalytic activity for the isomerization of olefins (*8*) and for the dehydration of methanol (*9*). Therefore, it seemed to be interesting to investigate in detail the hydroxyl groups in clinoptilolite as the possible active centers for catalytic reactions.

In the study of faujasite type zeolites, infrared spectroscopy was shown to be a pertinent technique for studying hydroxyl groups (*10*, *14*). This technique was used by Breger and Chandler (*3*) for the investigation of the surface of clinoptilolite. On natural clinoptilolite containing predominantly monovalent cations, they could not detect structural hydroxyl groups, but could discriminate between loosely and tightly held water molecules.

In this work, the properties of the hydroxyl groups of H-clinoptilolite are correlated with the catalytic activity for the isomerization of 1-butene.

EXPERIMENTAL

Materials

The clinoptilolite mineral used was from Tokaj, Hungary. The identification was made by Nemecz *et al.* (*11*). The sample contains 70–80% of clinoptilolite and about 15% of quarz, some feldspar and volcanic glass as impurities. The chemical composition of the natural mineral, the K^+ form and the H-form are shown in Table 1. The K-form was prepared from the original mineral by ion exchange with 2 *M* KNO_3 solution at reflux temperature followed by thorough washing. The NH_4^+ form prepared in the same way, using a 2 *M* NH_4NO_3 solution, was exchanged to about 70%. After washing, the samples were dried at 40°C. The NH_4^+ content of the sample was 1.3 mEq gm^{-1}.

The external surface area of clinoptilolite was determined by adsorption of Krypton at 78°K. The area was 26 m^2gm^{-1} for both the K- and NH_4-forms. The surface calculated from toluene adsorption at 104°C was 30 m^2gm^{-1} (*12*).

Ammonia was from J. T. Baker with a purity of 99.5%. The butene isomers were Fluka purum grade. The gases were dried and further purified using the freeze-pump-thaw technique. Pyridine was Uvasol grade from Fluka and was distilled in vacuo and dried over molecular sieve 5A before use.

Methods

For the catalytic experiments a conventional circulation reactor of the static type with a volume of 150 ml was used. Samples could be taken in a reproducible manner and were swept into the carrier gas of a gas chromatograph with catharometer detection. The products were separated at 25°C on a 7 m column, with an inside diameter of 2 mm and consisting of 30% dibenzylamine on chromosorb P. The amount of catalyst used was between 0.01 and 1.00 gm. The NH_4-clinoptilolite samples were pretreated in the reactor at temperatures between 200° and 800°C, using a vacuum of 10^{-3} Torr. The reaction temperature was 150°C and the butene pressure was 100 Torr. The rate of the reaction was calculated from conversion (in %)–contact time (in sec × gm × $mole^{-1}$) curves. These were linear up to a conversion of 15%. The cis/trans ratio was constant in this region.

The clinoptilolite samples used for infrared investigation were ground in an agate mortar. Platelets for spectroscopic use with a diameter of 25 mm and a thickness of about 10 mg cm^{-2} were prepared by compressing the samples at a pressure of 1.1 ton per square centimeter of film. The infra-

TABLE 1

CHEMICAL COMPOSITION OF THE SAMPLES

	Natural clinoptilolite			K-clinoptilolite			H-clinoptilolite		
	Weight %	$\frac{\text{Atom}}{\text{Si-atom}}$	$\frac{\text{Eq}}{\text{Si-atom}}$	Weight %	$\frac{\text{Atom}}{\text{Si-atom}}$	$\frac{\text{Eq}}{\text{Si-atom}}$	Weight %	$\frac{\text{Atom}}{\text{Si-atom}}$	$\frac{\text{Eq}}{\text{Si-atom}}$
SiO_2	77.15	Si: 1		76.46	Si: 1		81.58	Si: 1	
Al_2O_3	12.25	Al: 0.195		11.63	Al: 0.179		13.27	Al: 0.191	
Fe_2O_3	1.3	Fe: 0.012		1.16	Fe: 0.011		1.37	Fe: 0.012	
Na_2O	0.48		0.012	0.47		0.012	0.42		0.010
K_2O	5.06		0.084	9.34		0.156	3.05		0.048
MgO	0.64		0.025	0.55		0.021	0.10		0.004
CaO	3.10		0.087	0.37		0.010	0.20		0.005
$\frac{\Sigma \text{Eq}}{\text{Si-atom}}$			0.208			0.199			0.067

red cell used was fitted with CaF_2 windows and connected to a vacuum system. The spectra were recorded in the regions 1300–1700 cm^{-1} and 2600–3800 cm^{-1} on a Beckman IR12 double beam grating spectrometer. The scan speed for the spectra used in quantitative determinations was 20 cm^{-1} min^{-1}. The resolution was 1.5 and 2.6 cm^{-1} at 1350 and 3600 cm^{-1}, respectively. The transmission of the samples at 1350 cm^{-1} was 40%. For the spectra scanned at temperatures higher than 50°C, the rotating mirror after the sample was stopped to eliminate emission of radiation from the hot sample.

The NH_4-clinoptilolite disks were outgassed for 1 hr under a vacuum of 10^{-5} Torr. The temperature was raised slowly to the final outgassing temperature and held there for 1 hr. The samples were cooled to room temperature and spectra were scanned at this temperature. Ammonia was adsorbed at room temperature at a pressure of 20 Torr, followed by degassing at the same temperature. Pyridine (10 Torr) was adsorbed at 150°C for 1 hr and the excess was removed at the same temperature. The Brønsted and Lewis acid site concentration was estimated in the NH_3 adsorption experiments from the intensity of the δNH_4^+ band around 1440 cm^{-1} and the δNH_3 band at 1625 cm^{-1}, respectively. The adsorption of pyridine was also used to measure the Brønsted and Lewis site concentration. The bands at 1545 and 1450 cm^{-1} are used for the two kinds of sites, respectively. The adsorption coefficients of these bands are determined by carrying out the same adsorption experiments in a Mettler thermobalance on samples that contain only hydroxyl groups or Lewis sites (pretreated at 400° and 620°C, respectively). In this way the concentration of the Brønsted and Lewis sites could be determined fairly accurately ($\pm 5\%$).

The butene isomers were adsorbed in the infrared cell between 100° and 150°C at a pressure between 9 and 50 Torr. A spectrum was taken at reaction temperature, the frequency scale was locked at 3620 cm^{-1} (the maximum in the optical density of the hydroxyl groups), the butene isomer was adsorbed, and the decrease in optical density at 3620 cm^{-1} was followed as a function of the time. After equilibrium was reached, the sample was outgassed at the same temperature. Spectra were scanned at the temperature of adsorption after each step.

RESULTS

Surface Characterization

The wet NH_4-clinoptilolite samples lose H_2O and NH_3 molecules during the heat treatment at different temperatures. Figure 1 shows the infrared spectra of NH_4-clinoptilolite after pretreatment at 25°, 125°, 210°, 400°, and 550°C. The band at 1440 cm^{-1} corresponds to δHNH of NH_4^+ ions. The ν_{NH} bands are around 3200, 3050, and 2850 cm^{-1}. Residual water absorbs at 1625 cm^{-1} (δHOH) and at 3620 cm^{-1} (ν_{OH}). The band at 1440 cm^{-1} decreases upon heating and disappeared completely after outgassing at 400°C. The band at 1625 cm^{-1} decreases up to about 300°C. The residual peak at 1625 cm^{-1} remains nearly constant at higher pretreatment temperatures. After outgassing at 300°C a band starts to develop at 3620 cm^{-1}. This band is sharp, has a half band width of 68 cm^{-1} and is slightly asymmetric towards the lower wave numbers. A band at 3750 cm^{-1} is always present, indicating the presence of lattice terminating silanol groups or occluded silica particles.

In Fig. 2, the dehydration and deammoniation process is shown with the pretreatment temperature, based on the intensities of the bands at 1625 and 1440 cm^{-1}. For the NH_4^+ form the dehydration process is complete at 300°C, while for the K form residual water molecules are still held on the surface around 500°C. For the NH_4-form the deammoniation becomes important at 200°C. At 400°C NH_4^+ ions can no longer be detected. Readsorption of NH_3 on a sample, preheated at 400°C, shows the formation of NH_4^+ ions. Deammoniation of the latter sample is in no way different from the first heat treatment. Figure 2 shows that the deammoniation–ammoniation process is completely reversible under these conditions.

The hydroxyl concentration (3620 cm^{-1})

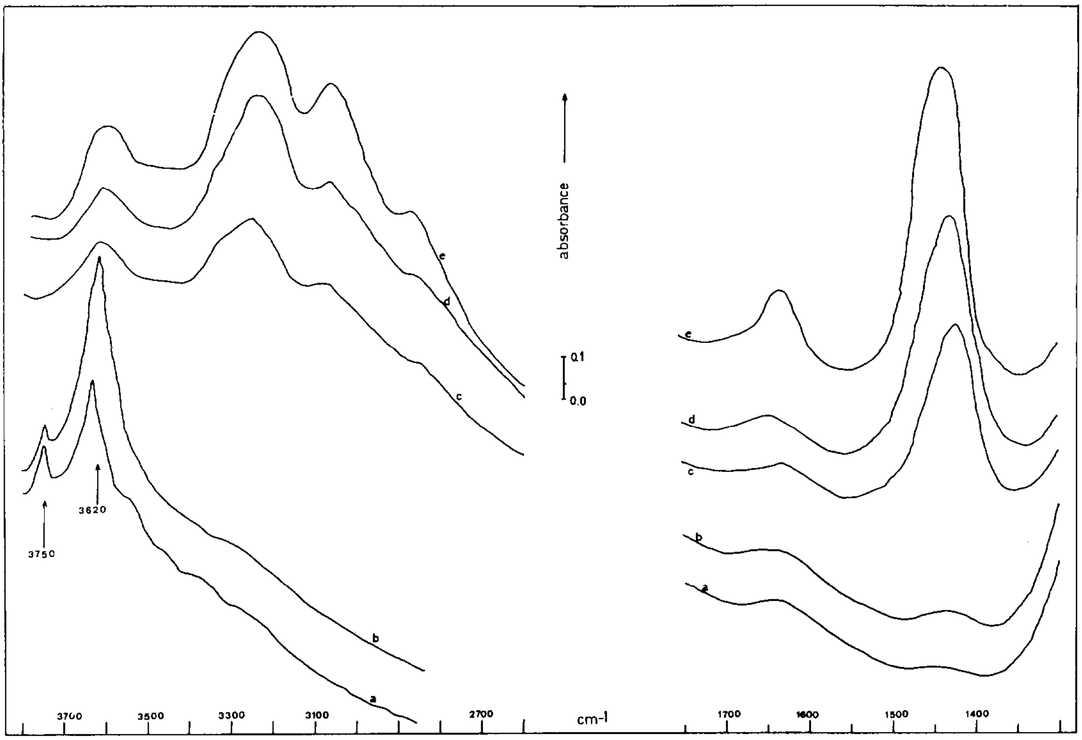


FIG. 1. Infrared spectra of NH_4^+-clinoptilolite outgassed at 25°C, (e), 125°C, (d), 210°C (c), 400°C, (b), and 550°C, (a).

is a maximum at 400°C and thereafter decreases linearly (Fig. 3A). When the NH_4^+ sample is heated in air at 400°C no substantial differences in frequency and intensity of the hydroxyl groups are observed. At each outgassing temperature the OH concentration calculated from the 3620 cm^{-1} band and from the 1440 cm^{-1} band upon readsorption of NH_3 molecules are in good agreement. In Fig. 3B it is shown that pre-

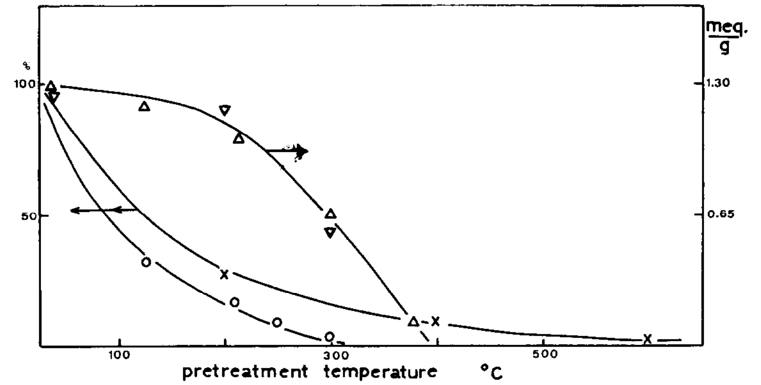


FIG. 2. Deammoniation and dehydration of the NH_4-form and dehydration of the K-form of clinoptilolite in vacuo as a function of the pretreatment temperature. (△), Change in intensity of the 1440 cm^{-1} band in NH_4^+-clinoptilolite. (▽), Change in intensity of the 1440 cm^{-1} band after readsorption of NH_3 on a sample, previously outgassed at 400°C. (○), Change in intensity of the 1625 cm^{-1} band in NH_4-clinoptilolite. (×), Change in intensity of the 1625 cm^{-1} band in K-clinoptilolite.

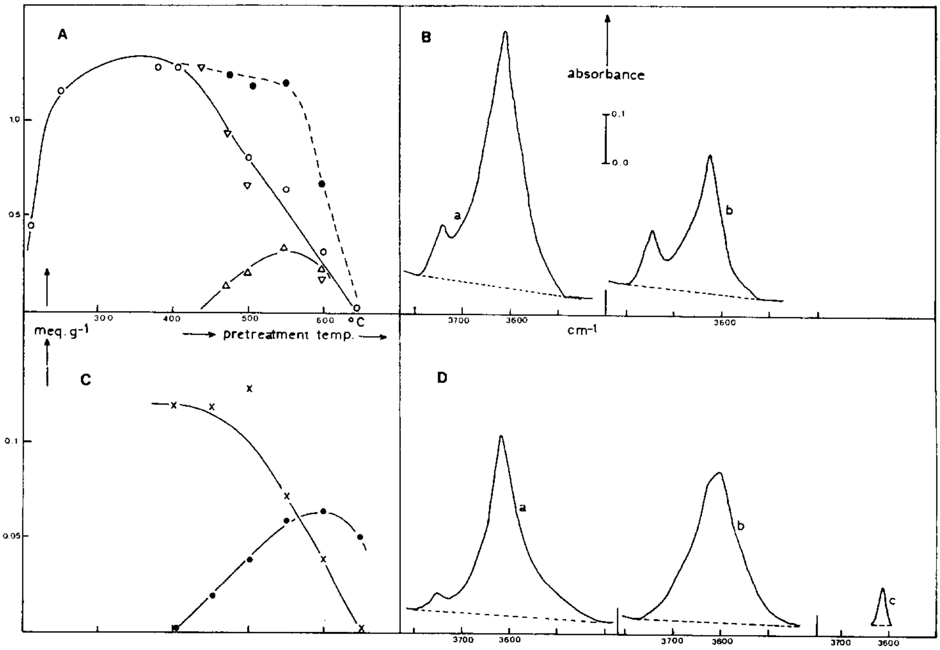


FIG. 3. Changes of the acidity of H^+-clinoptilolite with the pretreatment temperature. Part A. (○), hydroxyl band at 3620 cm^{-1}; (▽), Brønsted sites determined by room temperature adsorption of NH_3 (1440 cm^{-1} band); (△), Lewis site concentration (1625 cm^{-1} band of NH_3); (■), The sum of the Brønsted and twice the Lewis site concentration. Part B. The band shape of the hydroxyls at 3620 cm^{-1} after (a) outgassing at 400°C and (b) at 550°C. Part C. Adsorption of pyridine at 150°C on H-clinoptilolite at different pretreatment temperatures: (×) Brønsted pyridine (1545 cm^{-1}) and (●), Lewis-bonded pyridine (1450 cm^{-1}). Part D. The band shape of the hydroxyls: (a), after degassing at 400°C; (b), adsorption of pyridine at 150°C on (a); (c), the difference between (a) and (b).

treatment temperatures higher than 400°C significantly affect the band intensity, but not the band shape. At the same time as the hydroxyl groups disappear, Lewis sites appear as shown by the appearance of a band at 1625 cm^{-1} after NH_3 adsorption. This band shows a maximum at 550°C, followed by a decrease in the number of these sites.

After adsorption of pyridine only about 9% of the hydroxyl groups disappear. This is at variance with the behavior of NH_3. In Fig. 3D the behavior of the hydroxyls of a completely hydroxylated sample before and after pyridine adsorption is shown. Spectrum *c* is the difference between spectrum *a* and *b*. It is clear that pyridine molecules react with a well-defined part of the hydroxyl band. The concentration curve that gives the number of Brønsted and Lewis sites at higher pretreatment temperatures (Fig. 3C), shows the same changes as the total number of sites titrated with ammonia but their concentration is about one order of magnitude lower.

About 10 Torr of water was adsorbed at 25°, 200°, and 400°C on the sample pretreated at 550°C. In no case were changes in the hydroxyl peak at 3620 cm^{-1} observed. Lattice destruction seemed not to occur after this treatment.

Adsorption and Isomerization of n-Butenes

K-clinoptilolite has practically no activity for the interconversion of the three butene isomers. The activity of the NH_4^+-form rapidly increases with pretreatment temperature up to 300°C, remains constant to 450°C, and declines at higher outgassing temperatures. At 650°C the activity is less than 10% of the maximum value. The dependence of the rate of isomerization (r_{12})

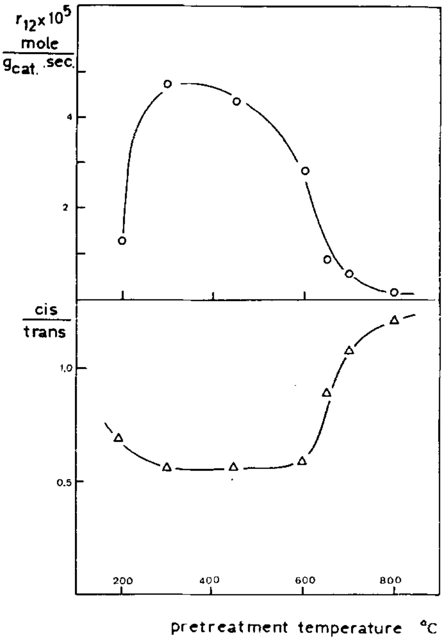


FIG. 4. The effect of the pretreatment temperature of NH_4^+-clinoptilolite on the catalytic activity (r_{12}) and selectivity (cis/trans ratio) of 1-butene isomerization.

of 1-butene into *trans*-butene on the pretreatment temperature is shown in Fig. 4. The same figure shows the corresponding changes of the cis/trans ratio. The ratio decreases slightly after deammoniation at higher temperatures, remains practically constant up to about 600°C and then rapidly increases.

In the region of temperature and pressure investigated, the cis and trans isomers adsorb rapidly on the H-clinoptilolite. The adsorption is complete after 1.5 to 2 minutes. The rate of adsorption of the trans isomer is two times faster than that of the cis-form. Figure 5 shows the hydroxyl groups before and after high temperature adsorption of *cis*-2-butene. Spectrum *c* is the difference between these two spectra. As in the case of pyridine adsorption, the hydroxyl groups that disappear show a narrow peak centered at 3620 cm^{-1}. At the temperatures investigated (100° and 150°C) the same amount (30%) of the hydroxyls is consumed, and the amount does not depend on the pressure of the reactant. The decrease of the optical density at 3620 cm^{-1} (Fig. 6) at different temperatures and pressures of butene shows a linear relation with $t^{1/2}$. Only a small amount of the butene adsorbed can be removed at the temperature of adsorption. The initial hydroxyl concentration is restored after outgassing at 400°C.

DISCUSSION

Nature of the Clinoptilolite Surface

The NH_4^+ bands in NH_4-clinoptilolite gradually decrease after outgassing at increasing temperatures. Within the sensitivity of the infrared method, the deam-

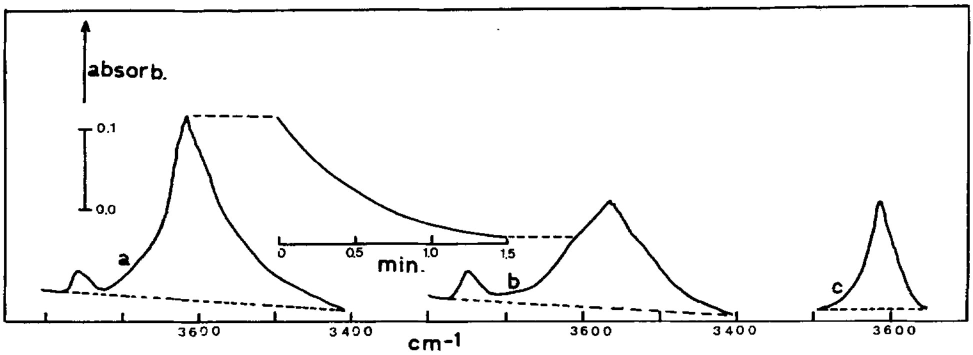


FIG. 5. The changes in intensity of the hydroxyl band at 3620 cm^{-1} during adsorption of *cis*-2-butene (25 Torr at 150°C): (a), the H^+-form outgassed at 400°C; (b), after adsorption; (c), the difference between (a) and (b). The insert between (a) and (b) shows the decrease of peak height at 3620 cm^{-1} as a function of time.

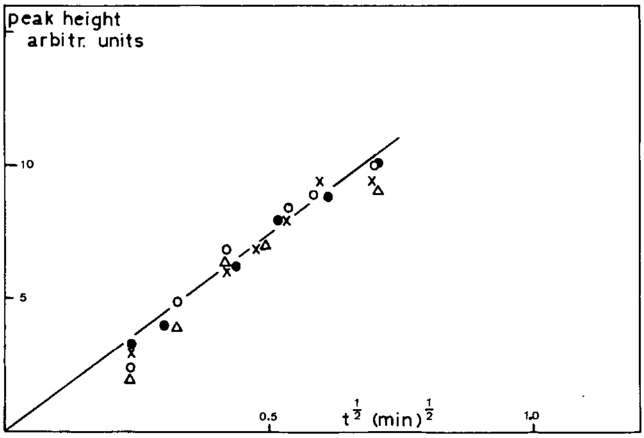
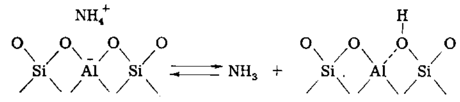


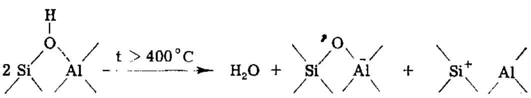
FIG. 6. The decrease in peak height of the 3620 cm^{-1} band on H^+-clinoptilolite outgassed at 400°C on adsorption of *trans*-2-butene as a function of square root of the time. (●), 100°C, 9 Torr; (△), 100°C, 24 Torr; (○), 125°C, 23 Torr; (×), 150°C, 25 Torr.

moniation seems to be complete at 400°C, and complete reammoniation is possible. This process may be schematised as follows:



The hydroxyl band formed at 3620 cm^{-1} is rather sharp and only slightly asymmetric to the lower wave numbers, indicating that to a great extent these groups are homogeneous in nature. Together with the deammoniation, most of the physically adsorbed water is evacuated at 300°C. The dehydration of the K-form is much slower and even at 600°C small amounts of water can still be removed. The K-clinoptilolite does not contain residual OH groups. Since H-clinoptilolite still contains K^+ ions, to an amount about 30% of those present in the K^+-form, it might well be that small amounts of physically held water are still present at temperatures higher than 300°C.

Above 400°C the surface hydroxyls decrease in intensity. At each temperature, the number of hydroxyls agrees very well with the number of protons that are capable of forming NH_4^+ ions. This means that the hydroxyl band at 3620 cm^{-1} (including the 3560 cm^{-1} hydroxyls) is the source of the Brønsted acidity in H-clinoptilolite. Above 400°C, as shown by the NH_3 titration, Lewis sites are formed at the expense of the hydroxyl groups. Up to 550°C, the sum of the hydroxyl concentration and twice the Lewis site concentration remains constant. The chemistry of the dehydroxylation can be written



Around 600°C, the number of Lewis sites is decreasing, too. At this temperature lattice destruction starts to occur. Readsorption of water at 200° or 400°C on a partially dehydroxylated sample does not restore the original OH concentration but neither does it produce lattice destruction. In contrast to hydrogen-Y zeolites (*14*) the hydrothermal stability of the H-clinoptilolite is higher. This is in agreement with the higher Si/Al ratio of the clinoptilolite as compared to the Y zeolite.

The dehydroxylation reaction was also followed by the adsorption of pyridine. With this method, similar changes in Brønsted and Lewis acidity as with NH_3 are observed. The number of Brønsted sites decreases and the number of Lewis sites increases up to 550°C. However, at each temperature not more than 10% of the number of sites titrated with NH_3 could be detected. Taking into account that ammonia is a stronger base than pyridine, this indicates clearly that pyridine molecules cannot enter the channel system of clinoptilolite and that therefore they characterize the Brønsted and Lewis sites on the external surface. At the same time it is shown that the external surface and the mass of the zeolite are hydroxylated and dehydroxylated at the same rate. The pyridine molecules react with a well-defined part of the hydroxyls (Fig. 3D). This amount is equal to about 0.1 mEq OH g^{-1}, absorbs at 3620 cm^{-1} (does not include the hydroxyls at 3560 cm^{-1}), and corresponds to the hydroxyl groups on the external surface.

After adsorption of butene in the temperature range used for catalytic conversion, about 0.4 mEq OH g^{-1} disappear. These hydroxyls absorb at 3620 cm^{-1} and the band has a half-band width of 35 cm^{-1}. These hydroxyls are probably the external hydroxyls and part of those located in the 7.05 × 4.25 Å channels. The resulting hydroxyls (70%) absorb at 3560 cm^{-1} and are probably distributed statistically over the three remaining types of channels. The thermal stability of the hydroxyls shows no difference with the location in the lattice.

Active Sites for the Butene Isomerization

The adsorption of butene on part of the hydroxyls seems to be controlled by the diffusion of the butene molecules in the 7.05 × 4.25 Å channels. Indeed, the amount of hydroxyls that disappear on butene adsorption does not depend on the temperature of the sample nor on the pressure of the reactant. If the process were a physisorption characterized by a low activation energy, infrared spectrometry would be too insensitive to characterize this. However, it seems more probable that the butene molecules enter the 7.05 × 4.25 Å channels. After the formation of a carbonium ion some oligomerization can occur. The oligomer formed cannot leave the channels at the reaction temperature. The decrease in hydroxyl concentration must therefore be due to a chemisorption process that is controlled by diffusion in the channels. This explanation is consistent with the observation that the rate of adsorption of *trans*-butene is greater than that of the *cis*-form. This explanation is supported by the fact that extrapolation of the conversion curves to zero contact time shows always about 1% conversion, although the starting material is a pure isomer. It is not excluded that oligomerization takes place also on the external surface. If the product can desorb easily from the external surface, the hydroxyl groups at this surface would not be poisoned to such an extent. Taking into account all these arguments, it seems that only the hydroxyl groups on the external surface, or a major part of them, are involved in the catalytic isomerization of butene over H-clinoptilolite. This is substan-

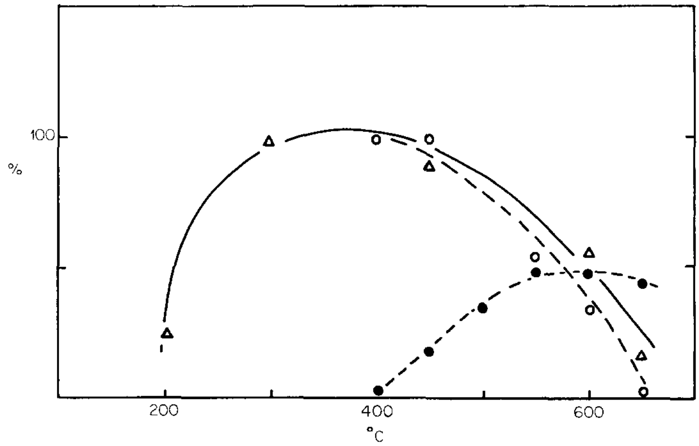


FIG. 7. Changes of r_{12} (△), Brønsted (○), and Lewis acidity (●) as titrated with pyridine, in relative units as a function of the pretreatment temperature of NH_4-clinoptilolite.

tiated by the data of Fig. 7. The Brønsted and Lewis acidity on the external surface are compared with the rate (r_{12}) in relative units. At each pretreatment temperature, there is a good agreement between the number of protons on the external clinoptilolite surface and the number of active sites. The selectivity of the reaction, as shown by the constant cis/trans ratio, is constant in the 300° to 600°C temperature region. This indicates that a certain number of active sites—external hydroxyl groups—is operative, the nature of which remains unaltered in the 300° to 600°C pretreatment region. The concentration of Lewis sites has no influence on the nature of the hydroxyl groups remaining at each temperature on the surface. This is in contrast to the situation on hydrogen Y zeolites, for which it was postulated that the Lewis sites can have an inductive effect on the hydroxyl groups and increase their acidity (*15*). Indeed on hydrogen Y zeolites it was found that the cis/trans ratio and activation energy starting from 1-butene changed with the pretreatment temperature (*16*).

At pretreatment temperatures above 600°C, lattice destruction starts and the selectivity of the catalyst changes. At the same time the activity is reduced considerably. This indicates that on the amorphous residue hydroxyls of a different nature show a slight residual activity. In view of this the possible influence of the impurities on the catalytic activity of the H-clinoptilolite should be considered. Since the K-form shows no isomerization activity, only the influence of the volcanic glass should be considered. These amorphous alumino-silicates can show a cation exchange capacity (*17*). However, butene isomerization on this kind of material shows a much lower conversion and a completely different selectivity (cis/trans = 1) (*9*). Therefore, the catalytic activity of the impurities can be neglected in the 300° to 600°C pretreatment region and the activity can be attributed exclusively to the hydroxyl groups on the external surface of the clinoptilolite which absorb in the infrared at 3620 cm^{-1}.

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REFERENCES

1. SCHALLER, W. T., *Amer. Mineral.* **17,** 128 (1932).

2. MUMPTON, F. A., *Amer. Mineral.* **45,** 350 (1960).

3. BREGER, J. A., CHANDLER, J. C., AND ZUBOVIC, P., *Amer. Mineral.* **55,** 825 (1970).

4a. MERKLE, A. B., AND SLAUGHTER, M., *Amer. Mineral.* **53,** 1120 (1968).

4b. MEIER, W. M., AND OLSON, D. H., *Adv. Chem. Ser.* **101,** 155 (1971).

5. BARRER, R. M., PAPADOPOULOS, R., AND REES, L. V. C., *J. Inorg. Nucl. Chem.* **29,** 2047 (1967).

6. AMES, L. L., *Amer. Mineral.* **45,** 689 (1960).

7. AMES, L. L., *Amer. Mineral.* **47,** 1310 (1962).

8. DETREKÖY, E., AND KALLÓ, D., "Symposium on Heterogeneous Catalysis," Varna, Bulgaria, 1971.

9. DETREKÖY, E., unpublished results.

10. JACOBS, P. A., AND UYTTERHOEVEN, J. B., *JCS Faraday I* **69,** 373 (1973).

11. NEMECZ, E., AND VARJÚ, GY., *Földtani Közl. Agyagásvány Füz.* **93,** 77 (1963).

12. PAPP, J., AND KALLÓ, D., *Magyar Kémiai Folyóirat* **75,** 3 (1969).

13. BARRER, R. M., AND MAKKI, M. B., *Canad. J. Chem.* **42,** 1481 (1964).

14. WARD, J. W., *Advan. Chem. Ser.* **101,** 380 (1971).

15. LUNSFORD, J. H., *J. Phys. Chem.* **72,** 4163 (1968).

16. DECLERCK, L. J., VANDAMME, L. J., AND JACOBS, P. A., *3rd Int. Conf. Molecular Sieves,* Zurich, September 1973, Recent Progress Report No. 168.

17. CAILLIÈRE, S., AND HÉNIN, S., "Minéralogie des Argiles," Chap. XII, p. 271. Masson et Cie., Paris, 1963.