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Surface and Some Catalytic Properties of a Germanic Near-Faujasite Molecular Sieve

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The germanic homologue of the silicic near-faujasite (Linde X) molecular sieve has been synthesized. The (cubic) unit cell parameter is 2.559 nm and the Ge/Al ratio is exactly unity. Per unit cell, the N_2, NH_3 and water adsorption isotherms are nearly identical with those obtained for the silicic Linde X zeolite.

A particular emphasis is placed on the infrared (ir) spectra of zeolite wafers having adsorbed H_2O, CO_2 and some organic reagents. The symmetric deformation of adsorbed NH_3 is observed in the 1100–1200 cm^{-1} region, suggesting interaction of the adsorbed species with the Na^+ cations.

The Na germanic sieve seems to have a stronger affinity for CO_2 than its silicic homologue. Several bands that can be assigned to "carbonate" surface species are observed between 1400 and 1600 cm^{-1}. It is suggested that the reaction of CO_2 with a lattice oxygen in a negatively charged Al tetrahedron could be responsible for the formation of the CO_3 group.

The OH stretching bands originating from the decationation of the ammonium sieve, or from those OH produced by a limited lattice hydrolysis are observed at about the same frequencies as in the silicic sieve. The main difference is in the greater instability of the Al–O–Ge linkage. This could be perhaps provoked by the relative instability of the fourfold coordination of Ge^{4+}.

On adsorbing methylacetylene in the presence of H_2, the reaction products are, at increasing temperature: allene and propylene between 200 and 300°C, acetone above 250°C. Below 200°C, the first important step shown by ir spectroscopy study is the formation of OH groups on a well-defined lattice position and of a surface propargyl group.

Dehydrogenation and dehydration of isopropanol into acetone and propylene have also been followed by glc and by ir spectroscopy. Especially interesting is the development of the C—C skeleton modes of vibration between 1150 and 1100 cm^{-1} and of the C=O deformation at 1240 cm^{-1}.

INTRODUCTION

A pure germanic near-faujasite has been synthesized at low temperature according to a procedure described elsewhere (*1*). This zeolite has been characterized by means of X-ray diffraction and its (cubic) unit cell parameter was found to be 2.559 nm. On the basis of chemical analysis, it was established that the Ge/Al ratio is near unity, e.g., higher than in the X Linde molecular sieve.

This contribution aims to describe some surface and catalytic properties of this germanic zeolite. A particular emphasis has been put on data derived from the infrared spectra of zeolite wafers having adsorbed NH_3, H_2O, CO_2, and some organic reagents at various temperatures. One main advantage of using the germanic sieve in infrared studies arises from the optical transparence in the 1050–1300 cm^{-1} region because the Ge–O stretching vibrations are below 1050 cm^{-1}.

It will be shown that opening of this spectral window sheds light on some reaction mechanisms in which skeleton C—C or C=O deformation vibrations are involved.

In spite of the fact that silicon and germanium have almost identical Pauling electronegativities, it seems that the properties of the Al—O—Ge or Al—$\overset{H}{\overset{|}{O}}$—Ge bonds are appreciably different from those in the silicic homologue. This will be illustrated here by several examples.

It should not be forgotten that with respect to oxygen, the preferred coordination of germanium is six. This is perhaps the reason why the Al-O-Ge is more fragile than the Al-O-Si linkage. This has significant consequences for the catalytic activity of the germanic sieve.

ADSORPTION ISOTHERMS

Adsorption isotherms for N_2, H_2O and NH_3 were obtained from a classical all-glass apparatus at −196, 20.5 and 21°C, respectively. The sample was pretreated at 200°C for 15 hr under a dynamic residual pressure of 10^{-6} Torr.

The gases used were of high purity. N_2 was further dried in a trap at liquid air temperature, NH_3 was distilled before use and H_2O was outgassed by the thaw-freeze procedure.

Only the sodium form has been studied. For the sake of comparison, these determinations were repeated under the same conditions on the Na-X Linde molecular sieve.

The results expressed as the number of molecules adsorbed per unit cell are shown in Fig. 1A, B and C with respect to increasing pressure. Obviously, the adsorption isotherms obtained for the germanic and silicic X sieves are almost identical suggesting a close similarity between their porous structures.

From the adsorption isotherms the porous volume could be approximated by using the amount of vapor occluded in the solid at the "B" point in the isotherm.

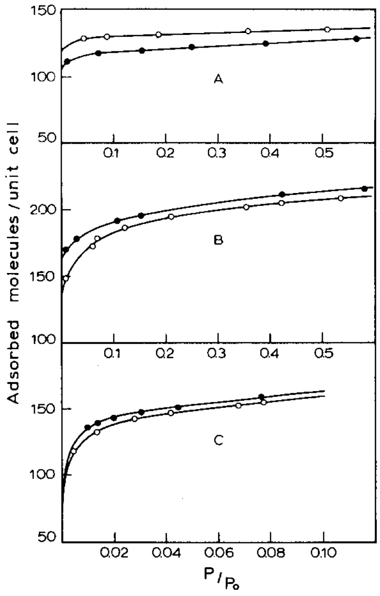


FIG. 1. Adsorption isotherms of (A) N_2 at −193°C, (B) H_2O at 20.5°C and (C) NH_3 at 21°C on Na germanic faujasite (●) and on Na-Linde X molecular sieve.

The results shown in Table 1 were obtained by using the density of the liquid at the temperature at which the adsorption measurements were performed.

In spite of the fact that water penetrates the sodalite cage while N_2 has access to the supercage only, the porous volume is smaller for water than for N_2. No satisfac-

TABLE 1

COMPARISON BETWEEN THE POROUS VOLUMES (cm^3/g OR liters/unit cell) OBTAINED FOR THE Ge AND Si SIEVES USING H_2O (AT 20.5°C), NH_3 (AT 21°C) AND N_2 (AT −196°C) AS ADSORBATES

	Ge sieve		Si sieve	
Adsorbate	cm^3/g	liters/u.c.	cm^3/g	liters/u.c.
H_2O	0.19	3.49	0.26	3.49
NH_3	0.20	3.58	0.26	3.49
N_2	0.22	3.94	0.33	4.43

tory explanation can be given to account for these differences.

INFRARED STUDY OF ADSORBED SPECIES

Procedure

Wafers of Na^+, Ca^{2+} and NH_4^+ germanic faujasite were prepared by the usual pressing technique. The weight of the wafers ranged between 10 and 15 mg/cm^2. The disc was introduced into the sample holder of an infrared Pyrex cell fitted with NaCl windows in which the wafer could be heated under vacuum at any desired temperature between 25 and 500°C. The spectra were scanned at room temperature on a Beckman IR 12 double beam grating spectrometer in the 1050–3800 cm^{-1} spectral region. The slit opening was such that the resolution at 3600 cm^{-1} was better than 5 cm^{-1}.

NH_3 ADSORBED ON THE GERMANIC ZEOLITE

Experimental Observations

As shown in Fig. 2 the adsorption of NH_3 by the anhydrous Na germanic sieve can be observed in the ir spectra by the presence of four bands, at 1178 and 1135 cm^{-1} and at 3370 and 3260 cm^{-1}, respectively. Gaseous NH_3 has ir absorption bands as follows: NH stretching split at 3335.9 and 3337.5 cm^{-1}, symmetrical deformation split at 931.6 and 967.1 cm^{-1} and the asymmetrical deformation at 1627.5 cm^{-1}. Wilmshurst (*2*) has shown that the frequency of the symmetrical deformation band is very sensitive to the electronegativity of the metal in ammine complexes. Frequencies at 1178 and 1135 cm^{-1} correspond roughly to electronegativities of 1.5 and 1.25, respectively. It may therefore be suggested to assign the two bands at 1178 and 1135 cm^{-1} to the symmetrical deformation of NH_3 coordinated to Na cations in two different lattice environments. As suggested by a referee, the two bands at 3370 and 3260 cm^{-1} might represent the N–H stretches of the two coordinated NH_3 species responsible for the 1178 and 1135 deformation bands. Indeed Little (*3*) quotes several examples taken from the literature which show that ammonia chemisorbed on Lewis acid sites of Vycor glass and of silicoalumina catalysts develops bands at 3365 and 3280 cm^{-1}. The asymmetrical deformation being weaker than the symmetrical one in coordination complexes [see, for instance, Nakamoto (*4*)], the band that should appear in the 1600 cm^{-1} region may overlap with carbonate bands. The latter is discussed in the next section.

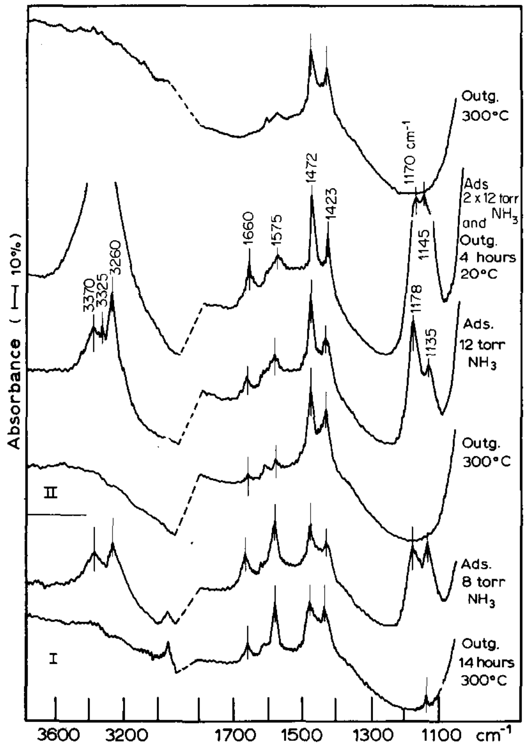


FIG. 2. Infrared spectra of NH_3 adsorbed on two different samples (I and II) of Na germanic zeolite at room temperature. The outgassing conditions are shown and the equilibrium pressures are 2 Torr (I) and 3 Torr (II). The sequence of the experiments is from bottom to top.

This first example of the ir study of molecules adsorbed by the germanic sieve demonstrates already the usefulness of the spectral window between 1300 and 1050 cm^{-1}.

INFRARED STUDY OF ADSORBED WATER AND CARBON DIOXIDE

The changes in the ir spectra in the OH stretching region at increasing temperature for the Na germanic zeolite are shown in Fig. 3A and B. In agreement with Bertsch and Habgood (*5*) the strong absorption band at 3690 cm^{-1} observed after outgassing at 100°C is assigned to OH groups of water coordinated to the Na^+ cations. A more extensive washing followed by outgassing at 100°C generates a strong band at 3590 cm^{-1} accompanied by a shoulder at 3650 cm^{-1}. The 3590 cm^{-1} band could result from a partial lattice hydrolysis in agreement with the assignment of a similar band in ultrastable zeolite by Jacobs and Uytterhoeven (*6*). Indeed, further washing causes a marked increase of this band. The shoulder at 3650 cm^{-1} is at the frequency observed for the OH arising from decationation. It may be therefore assigned to GeOH formed by the removal of some Na^+.

Two strong bands at 3340 and 3280 cm^{-1} represent the OH stretching of hy-

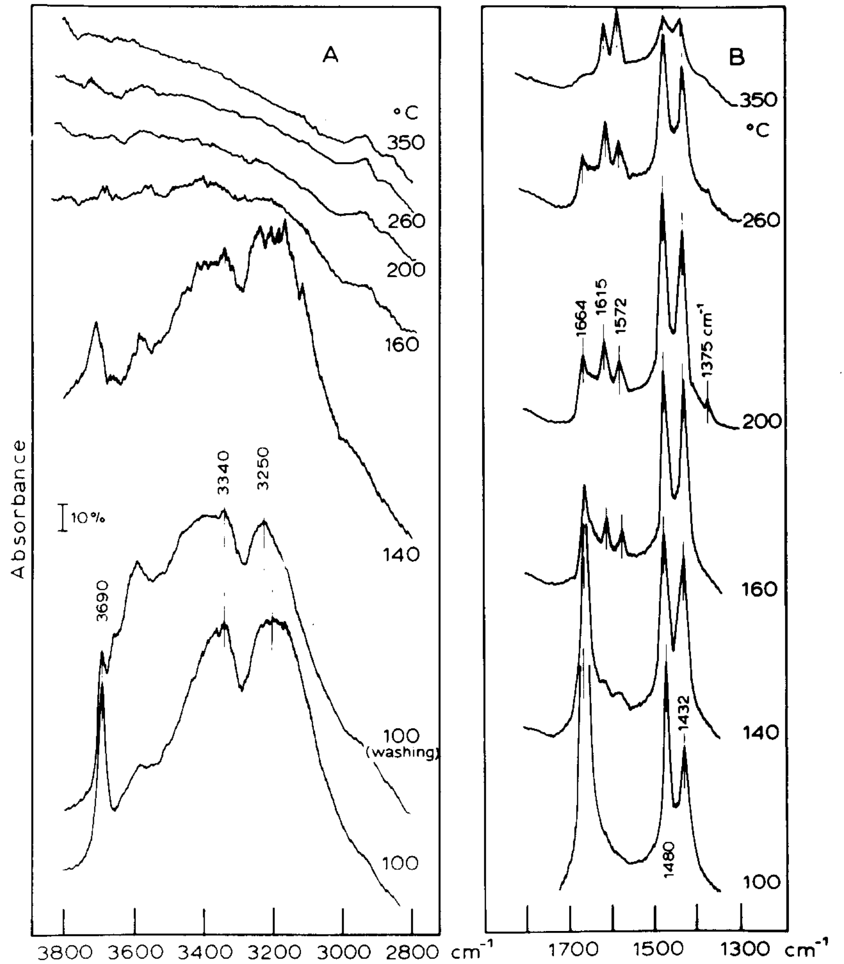


FIG. 3. Infrared spectra in the 3800–2800 cm^{-1} (A) and 1800–1200 cm^{-1} (B) regions of hydrated Na germanic zeolite heated for 2 hr at progressively increasing temperatures.

dration water. They disappear above 160°C. In slightly hydrated NaX zeolite similar bands are observed at 3400 and 3250 cm^{-1} (5). The deformation region between 1800 and 1300 cm^{-1} is shown in Fig. 3B. At 100°C and 140°C three narrow bands are observed at 1664, 1480 and 1432 cm^{-1}.

When the disc is heated at higher temperatures under vacuum, the intensity of the 1664 cm^{-1} band falls rapidly between 140 and 160°C, and slowly above 160°C. At 350°C, this band has almost disappeared while the two other bands at 1480 and 1432 cm^{-1} are much less pronounced. Simultaneously, upon heating, three bands develop at 1615, 1572 and 1375 cm^{-1} and increase slightly in intensity. At 350°C, the 1664 and 1375 cm^{-1} components have almost completely disappeared.

As shown in Fig. 3A, adsorbed water is removed approximately at 160°C. This means that the 1664 cm^{-1} band assigned to the H_2O deformation vibration overlaps probably with another band since it persists above this temperature. It may then be suggested that this band can be assigned to chemisorbed CO_2. This is discussed below.

NH_4-Na Germanic Zeolite

The special attention generally accorded to ammonium-exchanged zeolites is due to the fact that they are favored precursors of protonated lattices with a strong acid character.

Since it was found that the crystal structure is very sensitive to the exchange with NH_4^+ (*1*) only a sample with a low degree of exchange has so far been studied.

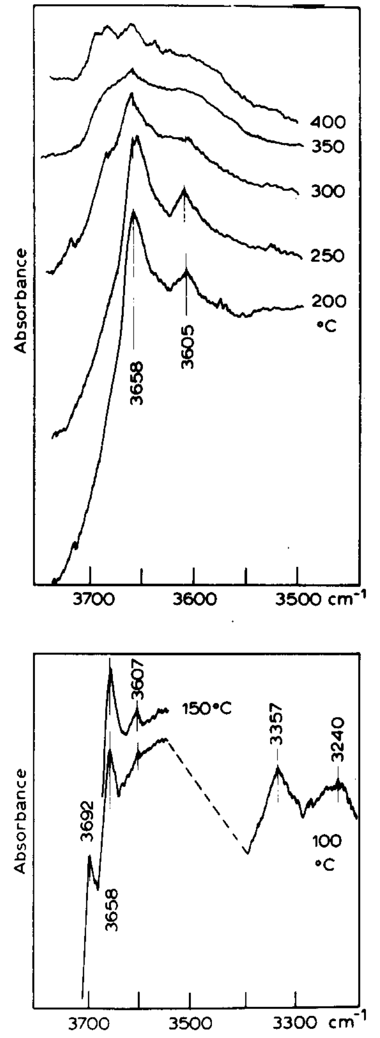
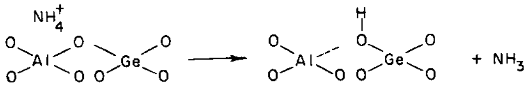


FIG. 4. Infrared spectra of two different wafers of the germanic zeolite partially NH_4^+-exchanged and heated at increasing temperatures.

Figure 4 shows the ir spectra corresponding to the OH stretching region of a zeolite sample in which 3% of the Na^+ has been exchanged by NH_4^+. Besides the band at 3690 cm^{-1} assigned, as in Fig. 3A, to the OH groups of water molecules polarized by the Na^+ cations, two strong absorption bands are observed at 3658 and 3605 cm^{-1}. The bands at 3357 and 3240 cm^{-1} are similar to those observed for the Na saturated sample although some NH stretching should show up in this region.

The band at 3658 cm^{-1} is assigned to OH groups produced upon decationation. In agreement with the findings of Uytterhoeven *et al.* (*7*), decationation could be depicted as follows:



The fact that on both the Ge and Si zeolites, this band appears at nearly the same frequency is not very surprising since the electronegativities of Si and Ge are the same [1.8 according to Pauling (*8*)].

The acid hydrolyzed fraction of the lattice could be responsible for the band at 3605 cm^{-1} in agreement with that observed after extensive washings (Fig. 3A).

In the 1200–1800 cm^{-1} region, only two bands are observed, at 1660 cm^{-1} and at 1465 cm^{-1}. The first corresponds to the deformation vibration of adsorbed water; whereas the second is due to NH_4^+. On heating this broad band disappears regularly but is not completely removed even at 400°C.

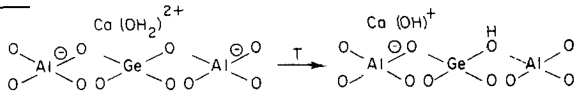
At no time is there any evidence for chemisorbed CO_2. This does not really mean that no CO_2 is present but if it is, the corresponding absorption bands must be either very weak or hidden in the NH_4^+ band.

Ca Germanic Zeolite

Figure 5A shows the OH vibration region of a partially Ca-exchanged disc (32%) heated at several temperatures.

Two main bands emerge near 3655 and 3520 cm^{-1}. Uytterhoeven *et al.* (9) and Ward (*10*) have shown that in silicic sieves the frequency of the absorption band at about 3590 cm^{-1} varies with the nature of the exchangeable cation: its location is a function of the strength of the electrostatic field. The analogy with our observations allows one to assign the 3520 cm^{-1} band to Ca $(OH)^+$ species.

The other absorption band near 3650 cm^{-1}, also observed in Fig. 3A and especially in the decationated form (Fig. 4), is similarly attributed to hydroxyls bonded to Ge tetrahedra. The general picture is then as follows:



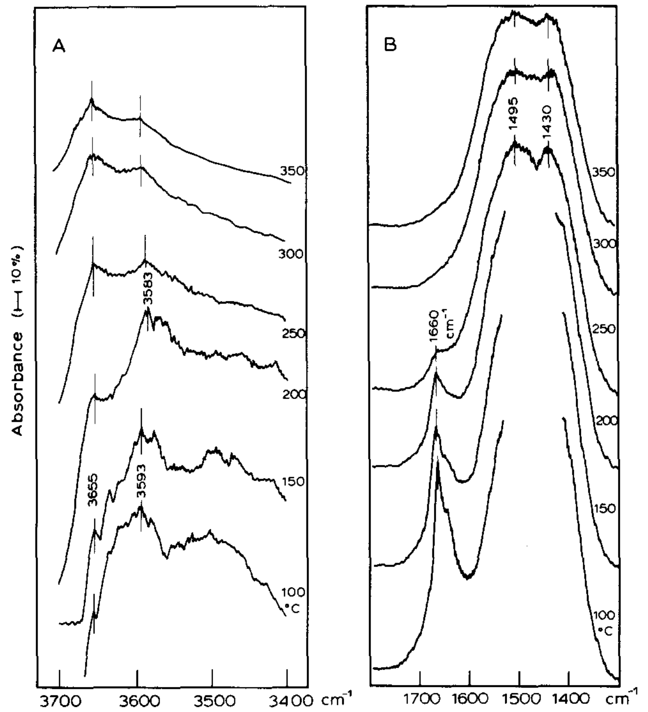


FIG. 5. Infrared spectra of 52% Ca-exchanged germanic zeolite heated at increasing temperatures in the 3700–3400 cm^{-1} (A) and in the 1800–1300 cm^{-1} (B) regions.

The broad band centered at about 3500 cm^{-1} could be due to zeolitic water molecules.

Figure 5B shows the spectra recorded in the 1200–1700 cm^{-1} region. Two bands appear on the disc heated at 100°C, respectively, at 1660 and near 1460 cm^{-1}. Upon further heating, the 1660 cm^{-1} band decreases in intensity and disappears almost completely above 200°C. The broad band at 1460 cm^{-1} decreases also with the heat treatment and shows two maxima at 1495 and 1430 cm^{-1}. In no case was a better resolution reached. This broad band is due to chemisorbed CO_2 with an almost symmetrical carbonate configuration.

SPECTROSCOPIC CHARACTERIZATION OF CHEMISORBED CO_2

The absorption bands that may be assigned to CO_2 chemisorbed by the Na germanic faujasite in the 1200–1800 cm^{-1} region are summarized in Table 2.

Chemical analysis made on both Na$^+$ and Ca^{2+} germanic faujasite have revealed 0.07 and 0.4% carbon contents, respectively. This means that, if all the C is assumed to correspond to the adsorbed CO_2 molecules, there is, in the Na germanic sample, one molecule CO_2 chemisorbed per 6 unit cells, whereas in the case of the calcium sample, one CO_2 molecule accommodates exactly one unit cell. This difference is clearly indicated by the respective intensities of the CO_2 bands in the ir spectra shown in Figs. 4B and 5B.

TABLE 2

CO_2 ABSORPTION BANDS (cm^{-1}) OBSERVED AT DIFFERENT TEMPERATURES (NA GERMANIC SIEVE, s: strong, w: weak, sh: shoulder)

Temp (°C)		
100°C	200°C	350°C
1664[a]	1664 (w)	–
–	1615 (w)	1615 (w)
–	1572 (w)	1572 (w)
1480 (s)	1480 (s)	1480 (w)
1432 (s)	1432 (s)	1432 (w)
–	1375 (sh)	–

[a] Overlapped with the H_2O deformation band.

Except for the 1664 cm^{-1} band, the absorption bands in Table 2 can be assigned to chemisorbed CO_2 with different configurations. The lack of evidence for a band near 1260 cm^{-1} rules out bidentate carbonate species (*11,12*). Taking into consideration the modification in the ir spectra with thermal treatment, it seems appropriate to suggest that the 1480 and 1432 cm^{-1} bands belong to the same carbonate species in agreement with the results obtained by Jacobs *et al.* (*13*) and by Bertsch and Habgood (*5*).

The assignment of the other bands is more difficult. The bands at 1615 and 1572 cm^{-1} have a similar "thermal" behavior at least till 260°C (see Fig. 3B). Therefore they might be characteristic of a single carbonate (or bicarbonate ?) species, in another environment. The reason why there is an inversion in the intensities at 350°C with the 1572 cm^{-1} band is not explained.

The 1664 and 1375 cm^{-1} bands disappear after heating at 350°C, which would also be an indication that they could be attributed to another less stable carbonate species, probably of the unidentate type. These bands, never observed on pure Na silicic sieves, have been reported, however, on partially Ca-exchanged samples (*13*).

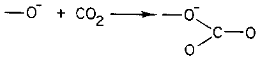
The bands in Table 2 disappear when Na$^+$ has been partially exchanged by NH_4^+ (<20%). The broad absorption observed in that case near 1465 cm^{-1} is the NH_4^+ deformation. This band decreases with decationation but is not completely removed after heating at 400°C. Even at a low extent, the Na$^+$–NH_4^+ exchange inhibits the formation of carbonate species, the OH groups probably being responsible for blocking the preferred sites for CO_2.

Chemisorption

Two very intense bands at 1480 and 1430 cm^{-1} are observed in the ir spectra of the Ca–Na-germanic sieve. They persist after heating at 300°C. No other band appears in the 1800–1200 cm^{-1} region. These bands are assigned to an almost symmetrical carbonate species. Such bands have been observed when a partially Ca-exchanged X zeolite sample is heated in the presence of CO_2 (*13*).

In conclusion, it seems that compared with the silicic homologues, the germanic zeolite behaves differently towards CO_2. Chemisorption of CO_2 as carbonate is perhaps favored by a higher number of exchange sites and/or by the presence of divalent cations such as Ca^{2+}. Indeed it has been shown elsewhere (*1*) that the Al/Ge ratio is never smaller than unity which means that the Al content is higher than in the Linde X molecular sieve. Secondly the presence of Ca^{2+} would create a higher number of less shielded sites. This would explain why more CO_2 is adsorbed on the Ca^{2+} partially exchanged sample.

It has sometimes been assumed that residual water molecules dissociated by the polarizing field of Ca^{2+} atoms are involved in the formation of a carbonate species (*9*). If this was correct, such species should also be formed on the surface of a Ca^{2+}-montmorillonite, where an enhancement of the water dissociation by six orders of magnitude has been recognized (*14*). However, when CO_2 is adsorbed on this surface, no carbonate is detected on the ir spectra (*15*). This observation suggests that lattice oxygens only are involved in the formation of carbonate, as schematized below:



where —O^- stands for an oxygen atom of a negatively charged Al tetrahedron.

ADSORPTION AND TRANSFORMATION OF ISOPROPANOL ON THE Na GERMANIC SIEVE

Isopropanol of spectroscopic purity has been adsorbed on a wafer made of the Na sieve pretreated in vacuum for 2 hr at 200°C; 1 Torr isopropanol was kept in the cell and the temperature of the wafer was increased progressively from 20 to 300°C. In a series of separate experiments, the transformation of isopropanol under similar conditions was studied in a batch reactor at 200 and 300°C.

Table 3 shows the reaction products observed by gas chromatography and expressed in mole percent. Propylene is the main product. Far behind in abundance, acetone, various C_4 aliphatic hydrocarbons and diisopropyl ether were the best represented species.

In Fig. 6 the ir spectra observed at various temperatures are shown. Below 148°C, the vibration bands of the zeolite framework (containing chemisorbed CO_2) and those that may be easily assigned to isopropanol are well defined. Especially interesting are those bands in the region between 1050 and 1300 cm^{-1} where the silicic sieves are blind because of the strong optical absorption due to the Si–O vibrations. Here the 1160, 1131 and 1114 (+2) cm^{-1} skeleton bands of the isopropyl group appear and are very well defined. The band due to the C–(OH) stretch overlaps probably with the 1160 cm^{-1} band while the OH deformation appears at 1312 cm^{-1}. Because of the "carbonate" bands, the 1350–1500 cm^{-1} region is very complex. However, the CH_3 deformation band should contribute to the 1378 cm^{-1} peak.

TABLE 3

REACTION PRODUCTS (MOLE%) FROM ISOPROPANOL, DETERMINED BY glc AFTER A REACTION TIME OF 2 HR ON THE NaGe SIEVE

Temp (°C):	200	300
Isopropanol	99.4	25.5
Acetone	0.04	4.1
Diisopropyl ether	0.09	1.8
Propylene	0.5	51.1
Saturated C_4	–	13.7
Unidentified	–	2.8

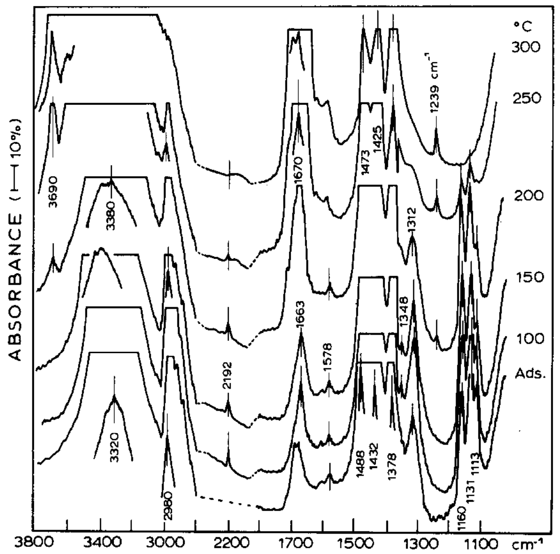


FIG. 6. Infrared spectra observed during the transformation of isopropanol (1 Torr) on Na germanic zeolite heated for 2 hr at increasing temperatures.

Above 100°C, the intensity of the isopropyl as well as of the OH deformation bands decreases progressively while a new band appears at 1238 cm^{-1}. A weak shoulder shows up at 1092 cm^{-1} at 300°C. Accordingly also the absorbance increases noticeably in the 1600–1700 cm^{-1} region and a shoulder at 1707 cm^{-1} is observed on the high frequency wing of this strong absorption band. Simultaneously, an OH stretching band develops at 3690 cm^{-1}.

These spectroscopic features can be easily explained by assuming that (1) isopropanol disappears, (2) acetone is formed by dehydrogenation of isopropanol, the 1707 cm^{-1} and 1238 cm^{-1} bands being the C=O stretching and deformation bands, respectively, and that (3) molecular water is produced by the dehydration of isopropanol into propylene. It contributes to the absorbance in the 1660 and 3690 cm^{-1} region.

There are no peculiar features that could be assigned to the main reaction product propylene, either because it does not remain adsorbed or that the C=C characteristic frequency overlaps with other bands.

A very interesting feature revealed by the spectroscopic study, as well by a separate set of experiments in which acetone was adsorbed by the same sieve, is the strong affinity of the surface for this molecule. Even so, a weak band is observed at 1238 cm^{-1} at 300°C in the presence of 1 Torr CH_3-CO-CH_3.

ADSORPTION AND REACTION OF METHYLACETYLENE ON THE Na GERMANIC ZEOLITE IN THE ABSENCE OR IN THE PRESENCE OF H_2

The infrared spectra obtained at increasing temperatures are shown in Fig. 7 for the reaction carried out in the presence of H_2. Each spectrum was taken after 2 hr standing under the specified conditions. The main reaction products identified in a batch reactor are shown in Table 4.

Immediately upon adsorption at room temperature an OH stretching band is observed at 3638 ± 1 cm^{-1}. This may well be a Ge–OH stretching somewhat shifted towards lower frequency because of the interaction with surrounding adsorbed species. This band is accompanied by a very strong and broad band between 3200

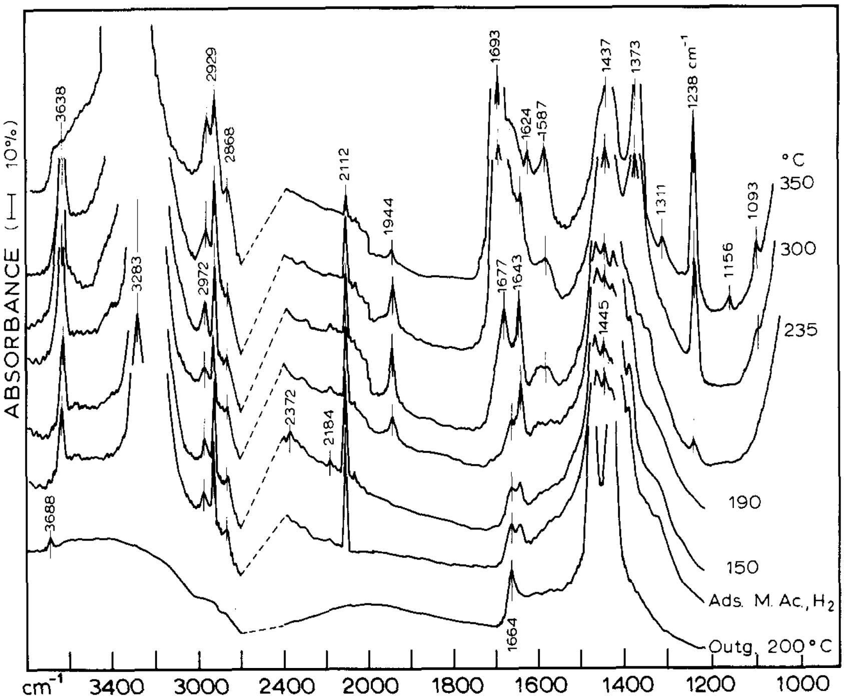
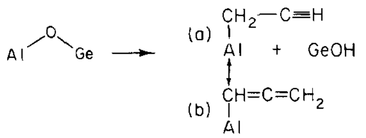


FIG. 7. Infrared spectra showing the reaction of methylacetylene (6 Torr) and hydrogen (20 Torr) on Na germanic zeolite heated for 2 hr at increasing temperatures.

and 3400 cm^{-1} (with a peak at 3283 cm^{-1}), by a narrow medium band at 2112 cm^{-1} and by a weaker band at 1643 cm^{-1}. Note that no band appears at about 1260 cm^{-1}. The formation of structural OH groups at room temperature could be explained in a way similar to that proposed by Chang and Kokes on zinc oxide:



In agreement with these authors, if the hydrocarbon fragment is essentially a propargyl anion $|CH_2—C\equiv CH|^-$, the two resonance forms (a) and (b) for the resulting hybrids can give rise to peculiar spectral features.

A possible objection to this model is that the propargyl residue might be linked to germanium as well, whereas the OH would be attached to aluminum. There are two main reasons in favor of the opposite picture, as suggested above. First, the energy of the C–Ge bond is at least 10 kcal lower than that of the C–Si bond and in silicic near-faujasite sieve a mechanism in which silicon could act as a Lewis site has never been observed. Second, the tendency for germanium to increase its coordination number is favored by the above mechanism since the OH is attached to it and a possible interaction of Ge^{4+} with the π electrons of the nearby double bond is not excluded.

TABLE 4

REACTION PRODUCTS (MOLE%) OBSERVED BY glc AFTER 2 HR REACTION OF 95 TORR METHYLACETYLENE AND 95 TORR H_2 IN THE PRESENCE OF THE NA GERMANIC ZEOLITE

Temp (°C):	200	300
Methylacetylene	88	70
Allene	–	20
Propylene	Tr	Tr
Acetylene	10	10

TABLE 5

FREQUENCIES (CM^{-1}) OF BANDS IN GASEOUS, LIQUID AND ADSORBED METHYLACETYLENE (*16–18*)[a]

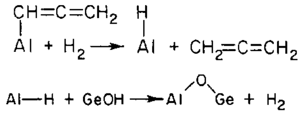
				I_{ads}		
				Al_2O_3		
Band	Assignment	R_{liquid}	I_{gas}	Weakly adsorbed	Strongly adsorbed	ZnO
ν_1	C—H	3305	3334	3300	–	3515 3250
ν_2	C—H	2926	2941	2935	2940	2920 2120
ν_3	C≡C	2123	2142	2120	2155	2080 1865
ν_4	CH_3	1382	–	1375	1375	1370
ν_5	C—C	–	926	–	–	–
ν_6	CH_3	2971	3008	2970	2970	2950
ν_7	CH_3	1448	1452	1460	1460	1440
$2\nu_7$	CH_3	2867	2881	2880	2880	2855
$2\nu_9$	δC≡C—H	–	1255	1260	1260	–
ν_3-$(\nu_9 + \nu_{10})$?		–	1187	–	–	–

[a] R_{liquid} = Raman; I_{gas} = infrared and I_{ads} = infrared spectrum of adsorbed methylacetylene.

The bands observed for adsorbed methylacetylene (*16,17*) are compared in Table 5 with those observed in the gaseous state (*18*). Above 150°C, a strong modification appears in the observed spectra. The 3638 cm^{-1} band increases in intensity, the 2112 cm^{-1} decreases and new bands develop at 2972, 1944 and 1643 cm^{-1}.

In the ir spectrum of gaseous allene, CH stretching is observed at 2972 cm^{-1} and C=C stretching at 1980 cm^{-1}, while a medium band is present at 1700 cm^{-1}. The strong CH_2 deformation band at 1389 cm^{-1} may be hidden in the highly absorbing region around 1400 cm^{-1}. The fact that the 1260 cm^{-1} C≡C—H deformation of methylacetylene is not observed at low temperature suggests that the (a) form shown above is not favored. The propargyl C=C=C stretching would then be at 2112 cm^{-1}.

At higher temperature, e.g., above 190°C, allene could be formed as follows:



$$\overset{CH{=}C{=}CH_2}{\overset{|}{Al}} + H_2 \longrightarrow \overset{H}{\overset{|}{Al}} + CH_2{=}C{=}CH_2$$

$$Al{-}H + GeOH \longrightarrow Al\overset{O}{\diagup\ \diagdown}Ge + H_2$$

The C=C=C characteristic stretching of adsorbed allene would be at 1944 cm^{-1}.

At about 235°C and above, new bands appear at 1238, 1092 and 1706 cm^{-1}, suggesting the formation of acetone. Accordingly the propargyl residues, as the chemisorbed allene, and the OH structural groups disappear as evidenced by the rapid decrease of the 3638, 2112 and 1944 cm^{-1} bands. The formation of acetone could result from the addition of a water molecule on the propargyl surface adduct, water being either of residual origin or formed by the reaction of H_2 with a lattice oxygen.

The band observed at 1643 cm^{-1} is characteristic of propylene.

In the absence of H_2, similar phenomena are observed but the formation of the OH groups as well as that of allene occur at a higher temperature. Moreover the forma-

TABLE 6
ABSORPTION BANDS OBSERVED IN THE REACTION OF METHYLACETYLENE WITH H_2 ON THE GERMANIC SIEVE

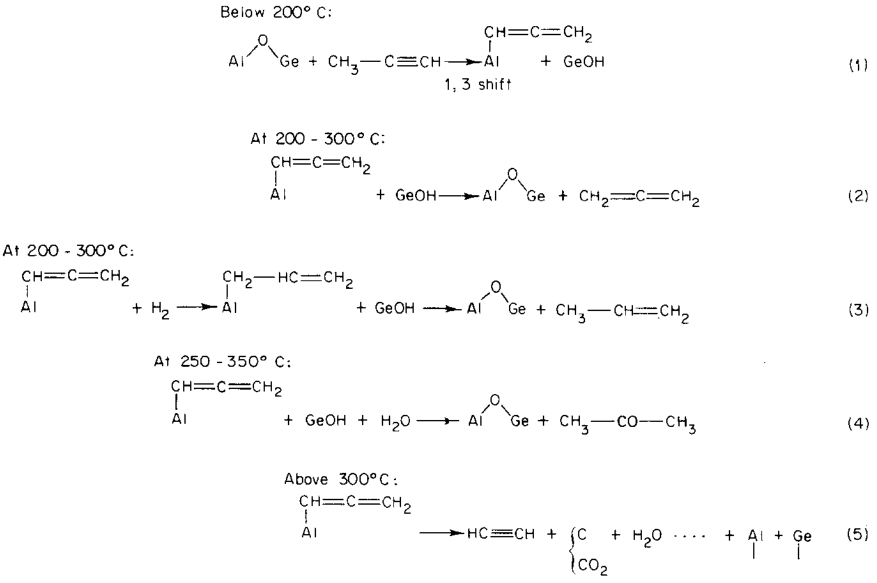
Surface species[a]	$CH{=}C{=}CH_2$	$CH_2{=}C{=}CH_2$(ads)	CH_3COCH_3(ads)	$CH_3{-}HC{=}CH_2$(ads)	$HC{\equiv}CH$(ads)
$\nu C{\equiv}C$					3300–3200
$\nu(C{=}C){-}H$	3300–3200	2972		2972	
$\nu(C{-}C){-}H$			2929	2929	
			2868	2867	
$\nu C{=}O$			1707		
$\nu C{=}C$ in allene or $C{\equiv}C$ in acetylene	2112	1944		1643	1944
$\delta{\equiv}C{-}H$					1330
$\delta{=}C{-}H$		1373	1350–1450	1377–1470	
$\delta{-}C{-}H$					
$\delta C{=}O$			1238		

[a] ν: stretching, δ: deformation.

tion of acetone and of propylene is much less pronounced.

As shown in Table 4, allene is by no means the only reaction product since acetylene is formed at 200°C, while allene is observed at higher temperature. According to Yates and Lucchesi (*17*), acetylene strongly held on alumina shows a CH and a C≡C stretching at 3300 cm^{-1} and at 2007 cm^{-1}, respectively, whereas for the same but weakly held adsorbed species, these bands are observed at 3220 and 1950 cm^{-1}, respectively. The assignment of the 1945 cm^{-1} band to adsorbed allene is therefore ambiguous.

In summary, the band assignment would be as shown in Table 6. The proposed reaction mechanisms are sketched below:



In addition, undefined polymerization reactions of allene and propylene could give rise to unassigned bands, especially in the C=C stretching region, while CO_2 could be responsible for the band at 2351 cm^{-1}.

ADSORPTION AND REACTION OF METHYLACETYLENE ON THE Ca GERMANIC ZEOLITE IN THE ABSENCE OF H_2

Adsorption of methyl acetylene by the Ca sieve results probably in the opening of the Al–O–Ge bridge, as shown by reaction (1) above. As shown in Fig. 8, bands are indeed observed at 3280 and at 2112 cm^{-1} while the 3638 cm^{-1} GeOH stretching appears as a shoulder on the high frequency wing of the broad OH band already present before adsorption. Between 100 and 200°C two new bands are observed at 2183 and 1946 cm^{-1}. The latter may be due either to allene or to acetylene. According to Table 6, the formation of acetylene seems more probable because of the absence of the $\nu(C{=}C){-}H$ band at 2972 cm^{-1}. In addition, the cracking of the propargyl group followed by the pyrolysis of the hydrocarbon residues could account for the band at 2183 cm^{-1}, assuming that it is due to a GeH stretching band. Such a band has been observed in amorphous germania at 2180 cm^{-1} (*19*) and in n-Ge_4H_{10} at 2080 cm^{-1} (*20*).

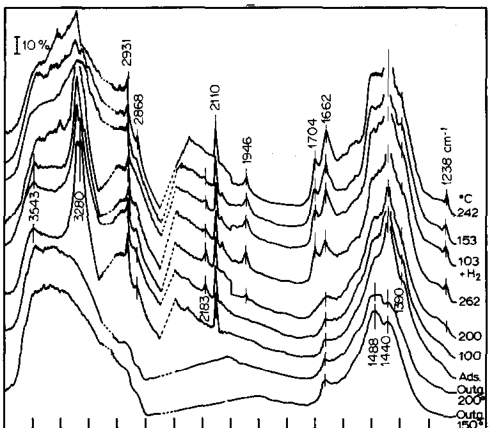


FIG. 8. Infrared spectra showing the transformation of methylacetylene (8.5 Torr) on a Ca disc heated for 2 hr at increasing temperatures, and after addition of 9 Torr H_2.

Above 200°C and in agreement with reaction (4), small amounts of acetone are formed.

The 1662 cm^{-1} band in Fig. 8 and the increase in intensity observed for the broad band at 3200–3300 cm^{-1} may well be the deformation and stretching bands of H_2O.

DISCUSSION

Facing the task of characterizing the surface and the catalytic properties of a new type of active solid, a choice had to be made between various methods able to provide the most significant data. Here the adsorption isotherms of a nonpolar (N_2) and of polar (H_2O and NH_3) molecules have shown that from the viewpoint of the extent of the surface area and of the pore volume, the germanic near-faujasite zeolite (with $Al/Ge = 1$) behaves in a similar manner as its silicic homologue. Also the frequencies at which the stretching GeOH bands are observed are almost identical with those reported for the silicic molecular sieve Linde X. This similarity is probably due to the fact that Ge and Si have the same Pauling electronegativity. However, the Ge–O stretching band, because of the mass effect, is below 1050 cm^{-1}. This constitutes a favorable circumstance because it opens a spectral window on an unexplored region in the study of molecules adsorbed by aluminosilicates.

A more fundamental difference between the germanic and silicic near-faujasite zeolites is the greater instability of the Ge–O–Al linkage. This could be due to the favored sixfold coordination of germanium with respect to oxygen. This may give rise to an interesting surface activity such as that observed in the reaction with methylacetylene, leading to the formation of propargyl and of GeOH surface groups. The surface propargyl group may be involved in hydrogenation or hydration reactions.

Along the same vein the strong interaction with CO_2 could also well be an indication of the tendency for germanium to transfer from the fourfold to the sixfold coordinated state.

On several occasions the formation of Ge–H bonds has been suspected. This seems to occur readily when pyrolysis of carbon residues occurs on the surface at very moderate temperature. The conditions of formation of Si–H bonds is far more critical, as shown by Morterra and Low (*21*,*22*).

In the above comparison the possibility for germanium to exist in two valency states, namely Ge^{4+} and Ge^{2+}, does not appear to exert a determining role in the catalytic properties. However, the interaction of molecules or of chemical groups containing π electrons with Ge^{4+} could be favored to some extent by this trend. This might perhaps explain surface reactions in which adjacent Al and Ge interact simultaneously with the same organic reagent, as could be the case with methylacetylene.

Because of the fragility of the Al–O–Ge linkage, the Ge sieve is a less acid catalyst than its silicic homologue. Unpublished data have shown, for instance, that at 200°C a germanic sieve in which 73% of the initial Na^+ cations have been replaced by Ca^{2+} has the same activity in dehydrating *tert*-butanol as the corresponding Ca-exchanged silicic sieve at lower temperature, let us say at about 150°C.

It may thus be concluded that in spite of their textural and structural resemblance, the germanic and silicic near-faujasite (X) zeolites have different surface and catalytic activities; the origin of this difference is on the one hand the tendency for germanium to be sixfold coordinated with oxygen and on the other hand the existence of a lower state of oxidation, e.g., Ge^{2+}.

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