JOURNAL OF CATALYSIS 52, 321–331 (1978)

An Infrared Study of the Surface Acidity of Germanic Near-Faujasite Zeolite by Pyridine Adsorption

G. PONCELET AND M. L. DUBRU

Groupe de Physico-Chimie Minérale et de Catalyse, Université Catholique de Louvain,
Place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

Received June 24, 1977

The acidic properties of germanic near-faujasite zeolite have been investigated by pyridine adsorption measurements on the sodium, calcium, and partially protonated forms. As for the silicic X and Y analogs, no acidity could be detected on Na–GeX. In contrast to the silicic sieves, a 73% calcium-exchanged sample did not show the ir band at 1540 cm^{-1} characteristic of pyridine in interaction with Brønsted acid sites. The fact that residual water molecules are not dissociated to a measurable degree on the germanic sieve has been attributed to the Al content of this sieve, which is higher than in the X and Y homologs. Both Brønsted and Lewis acid centers were found on partially protonated germanic faujasite, but the weak interaction of pyridine with those sites indicates an acid strength lower than in the silicic homologs. The weak overall acidity of the germanic sieve is consistent with the lower activities and higher selectivities when this solid is used as a catalyst in the isomerization reaction of the *n*-butenes.

INTRODUCTION

In a previous study, preliminary data on the surface properties and some catalytic properties of the germanic homolog of near-faujasite have been reported (*1*, *2*). In this zeolite, where all structural silicon atoms are replaced by Ge atoms, the Ge/Al ratio is unity, i.e., slightly lower than the Si/Al ratio of the silicic X type. Its cation content is 5.4 meq/g, and the unit-cell parameter is 25.59 Å, which is larger than the values given for the Linde X and Y zeolites (*3*).

In contrast to its silicic homologs, the germanic faujasite has no activity in cumene cracking, and propylene produced during the dehydration of isopropanol does not polymerize.

Recently (*4*) the isomerization of *n*-butene over protonated germanium near-faujasite was studied, and the results were compared to those obtained on protonated X and Y and partially dealuminated Y zeolites. The kinetic parameters were found to be in favor of a mechanism implying the formation of a common intermediate, the s-butyl carbonium ion. No deactivation due to secondary polymerization reactions occurred on the germanic sieve. From the relationships between the 2:1 product ratios, the turnover numbers and the absorption frequencies of the supercage OH groups versus the Si (or Ge)/Al ratio, it was concluded that the acid strength of the Brønsted sites increased as the aluminum content of the zeolite decreased.

Infrared spectroscopy of adsorbed bases has been shown to be very suitable for the characterization of the surface acidity of solids. Pyridine has been widely used as a probe to differentiate Brønsted acidity from Lewis acidity (*5*) and to quantify these

0021-9517/78/0522-0321$02.00/0
Copyright © 1978 by Academic Press, Inc.
All rights of reproduction in any form reserved.

types of surface acidity (*6–10*). Recent reviews on the subject have been published by Ward (*11*) and Jacobs (*12*).

The present work was undertaken in order to establish the nature of the surface acidity of the germanic near-faujasite zeolite and to compare its acidic properties with those of the silicic X and Y homologs. This paper reports an ir study of pyridine adsorption on the Na, Na–Ca, and Na–H forms.

EXPERIMENTAL

Material. Germanic near-faujasite zeolite was synthesized from Al–Ge gels with an initial molar composition GeO_2:Al_2O_3:Na_2O of 9:3:8, according to the procedure explained elsewhere (*13*). In a typical synthesis, a gel was prepared by dissolving the corresponding weight of metallic Al (as powder, Merck, p.a.) in NaOH; GeO_2 (electronic purity, from Hoboken) was then dissolved in the solution. The final liquid to solid ratio of the reacting gel was 4. The reactants were introduced in Teflon containers, which were hermetically closed and placed in an oven. The synthesis was carried out at 90°C for 40 hr. The solid was washed several times with distilled water and dried at room temperature.

The NH_4- and Ca-exchanged samples

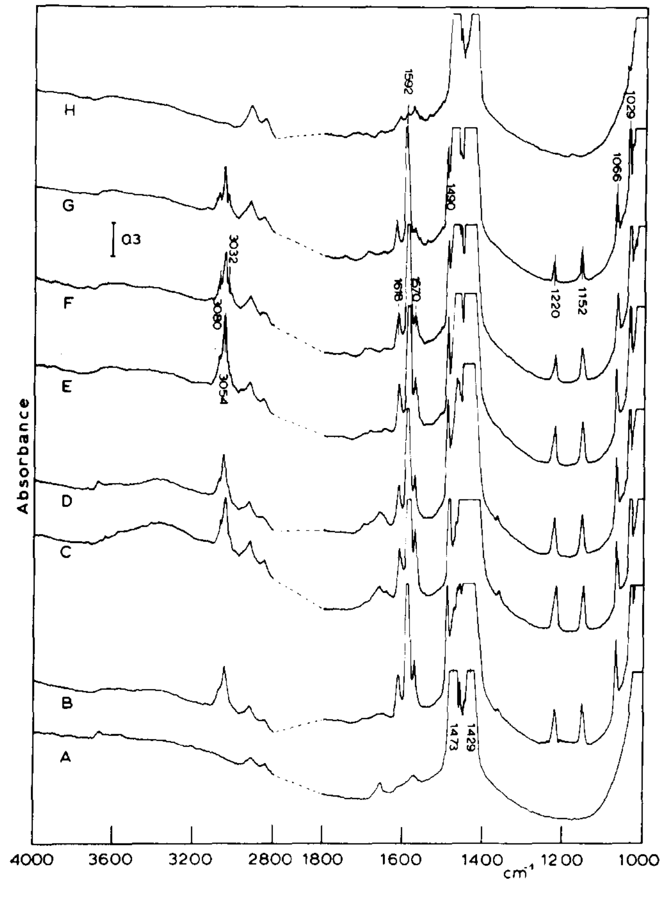

FIG. 1. Pyridine on Na–GeX. A, After outgassing at 300°C for 15 hr; B, adsorption of 1.5 μmol of pyridine; C, adsorption of 3 μmol of pyridine; D, desorption at room temperature for 1.5 hr; E, outgassing at 100°C for 1.5 hr; F, evacuated at 150°C, 1.5 hr; G, evacuated at 200°C for 1 hr; H, evaluated at 230°C for 12 hr.

were prepared using 0.2 N acetate solutions. The crystallinity of the different samples was checked by X-ray diffraction analysis.

Sample preparation and apparatus. For the spectroscopic studies, self-supporting disks (10–15 mg/cm^2) were prepared by compressing small amounts of the zeolite in a stainless-steel die, under a pressure of 300 kg/cm^2.

Infrared spectra were recorded in absorbance using a Perkin-Elmer 180 spectrophotometer carefully set to make instrument errors negligible.

The disk was placed in the sample holder and introduced into an ir Pyrex cell fitted with NaCl windows. The cell could be attached to a conventional vacuum apparatus.

Technique. The wafer placed at the bottom of the cell could be heated in vacuum at any desired temperature. Generally, the temperature was slowly raised to 100°C and maintained for several hours until a residual pressure of approximately 10^{-4} Torr was attained. Afterwards, the temperature was slowly raised to 300°C, and the sample was evacuated at this temperature for 15 hr. It was then cooled to room temperature, and the ir spectra were recorded. Pyridine was introduced into the cell and 30 min were allowed for the adsorption to reach equilibrium. The spectra were recorded after adsorption and after outgassing the sample at different temperatures.

Pyridine was purified by two successive distillations over P_2O_5 and stored in a glass bulb containing a 5A molecular sieve. Each distillation was carried out under vacuum, using a liquid nitrogen trap to condense the product.

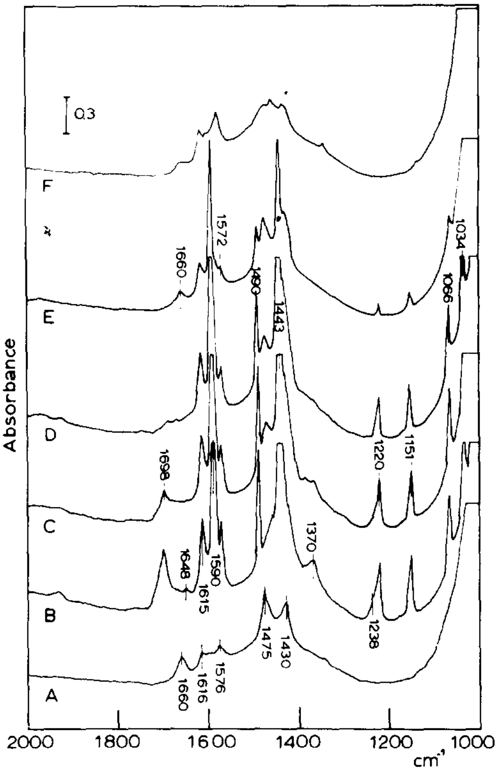

FIG. 2. Pyridine on Na–GeX. A, Evacuation at 300°C; B, adsorption of 2 μmol of pyridine; C, evacuated at 100°C, 2 hr; D, evacuated at 150°C, 1.5 hr; E, evacuated at 250°C, 2 hr; F, evacuated at 300°C, 15 hr.

RESULTS

Figures 1 and 2 show the ir spectra obtained on two samples of Na–GeX. Spectrum A in Fig. 1, referring to the wafer outgassed at 300°C for 15 hr, shows two bands at 1473 and 1429 cm^{-1}. When the outgassing is carried out at the same temperature for 24 hr, additional bands develop at 1660, 1616, 1575, and near 1350 cm^{-1}. The pairs of bands at 1473–1429 and 1616–1575 cm^{-1} have been discussed in a previous study (1) and attributed to chemisorbed CO_2 in two different configurations.

When pyridine is adsorbed on Na–GeX (spectra B and C in Fig. 1), several bands appear at 1618, 1592, 1570, 1490, 1220, 1152, 1066, and 1029 cm^{-1}, and at 3080, 3054, and 3032 cm^{-1}. Desorption at room temperature (D) and at increasing temperatures (spectra E to H) results in the progressive disappearance of all the bands. After outgassing at 230°C for 12 hr,

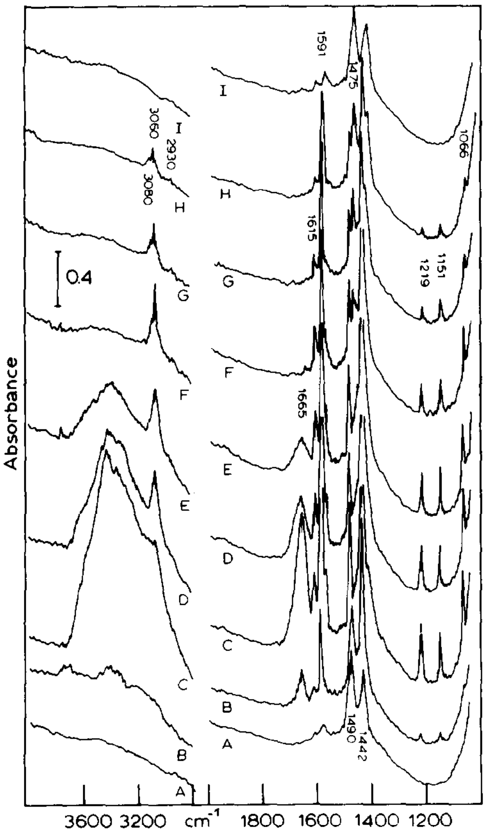

FIG. 3. Pyridine and H_2O on Na–GeX. A, after evacuation at 300°C for 4 hr; B, adsorption of 1.2 μmol of pyridine; C, adsorption of 5 μmol of pyridine; D, after outgassing at room temperature; E, evacuated at 60°C for 2.5 hr; F, evacuated at 125°C, 2 hr; G, evacuated at 175°C, 2 hr; H, evacuated at 225°C, 2 hr; I, evacuated at 275°C, 8 hr.

pyridine is completely removed and the initial spectrum is restored. The bands near 2950 and 2840 cm^{-1} are due to some surface contamination by organic material from the vacuum grease in the system.

Figure 1 also shows that upon adsorption of pyridine, the intensity of the band at 1473 cm^{-1} diminishes, whereas the band at 1429 cm^{-1} is reinforced. This phenomenon is reversible. According to Jacobs *et al.* (*14*), who discussed the presence of these CO_3^{2-} bands in terms of the symmetry of sites SII and SIII′, the spectral modifications due to pyridine seem to indicate that some rearrangement of the CO_3^{2-} in the supercage occurs, conferring a higher symmetry to the carbonate species on sites SIII′, or that CO_2 is moved toward the sites SII, due to higher affinity of pyridine for the sites SIII′.

A similar change is observed in the sequence of spectra shown in Fig. 2. However, upon adsorption of pyridine (B), additional bands develop at 1698 and 1370 cm^{-1}, while the pyridine band at 1443 cm^{-1}, overlapping with the CO_2 band at 1429 cm^{-1} in Fig. 1, is clearly distinguished. A similar effect of pyridine on the bands at 1475–1430 cm^{-1} of chemisorbed CO_2 is observed.

A slight difference is found after removal of pyridine at 300°C (F); indeed, the bands at 1616–1575 cm^{-1} show an increase in intensity, whereas those at 1475–1430 cm^{-1} are slightly less developed.

The spectra of Fig. 3 have been obtained upon adsorption of pyridine (6 μmol) in the presence of a small amount of water (B and C). Adsorbed water is responsible for the band at 1665 cm^{-1} and for the broad absorption near 3400 cm^{-1}. A similar evolution in the spectra is observed upon progressive desorption of pyridine at increasing temperatures (spectra D–H). The initial spectrum is restored after complete removal of pyridine. In this case also, adsorbed pyridine enhances the symmetry of the chemisorbed CO_2. An interesting point in this figure is that adsorbed water molecules are readily removed upon mild thermal treatment. Indeed, an outgassing at 125°C for 2 hr (spectrum E) is sufficient to remove all adsorbed water. In the absence of pyridine, hydration water molecules are eliminated only after heating in vacuum at 260°C for several hours (*1*).

Pyridine was adsorbed on a partially ammonium-exchanged germanic sieve (17% NH_4). The sequence of treatments and the corresponding ir spectra are shown in Fig. 4. Spectrum A of this figure, referring to the disk outgassed for 15 hr at 230°C

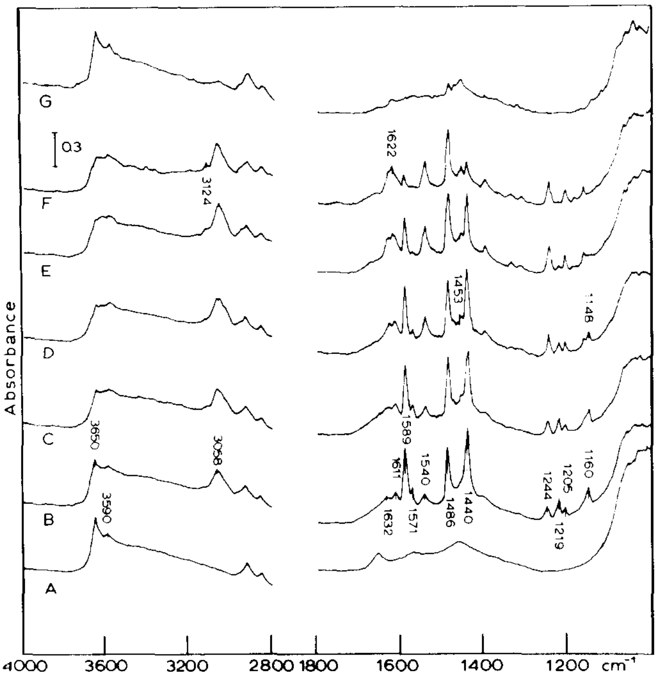

FIG. 4. Pyridine on NaH–GeX (17% exchanged). A, Outgassed at 230°C, 15 hr, then at 300°C, 1 hr; B, adsorption of 0.75 μmol of pyridine; C, desorption at room temperature, 3 hr; D, evacuated at 105°C, 1.5 hr; E, evacuated at 150°C, 1.5 hr; F, evacuated at 195°C, 1 hr; G, evacuated at 240°C, 10 hr.

and then for 1 hr at 300°C, shows two bands in the OH stretching region, at 3650 and 3590 cm^{-1}, due to the surface protonation occurring upon decationation (*15*). It is seen that the bands of chemisorbed CO_2 are completely absent in the spectrum, whereas they were always found on Na–GeX.

Upon adsorption of 0.75 μmol of pyridine (spectrum B), two series of bands appear. The first group contains those at 3058, 1611, 1590, 1571, 1486, 1440, 1224, 1219, and 1148 cm^{-1} which were found on Na–GeX. The second group contains the bands at 1630, 1540, 1244, 1205, and 1160 cm^{-1}. The adsorption of pyridine produces a diminution in the intensity of the 3650-cm^{-1} band and does not affect the 3590-cm^{-1} band.

Evacuation of the cell at room temperature for 3 hr (spectrum C) does not appreciably modify the spectrum; only the bands at 1587 and 1440 cm^{-1} slightly diminish, and the shoulder near 1453 cm^{-1} is more visible.

After outgassing at 105° for 3 hr (spectrum D), a significant increase in the intensity of the bands at 1540, 1244, 1205, and 1160 cm^{-1} is observed. Outgassing at increasing temperatures (spectra E and F) reinforces this change. During this sequence of thermal treatments, the absorption band at 3650 cm^{-1} shows an inverse behavior, decreasing with temperature.

In spectrum F (after outgassing at 195°C for 1 hr), the less intense bands at 1611, 1571, 1219, and 1148 cm^{-1} are no longer found, and those at 1590 and 1440 cm^{-1} are much less developed. The band at 3124 cm^{-1}, though weak, is more visible. The initial spectrum is recovered when the wafer has been evacuated at 240°C (spectrum G).

The spectra of Fig. 5 have been obtained

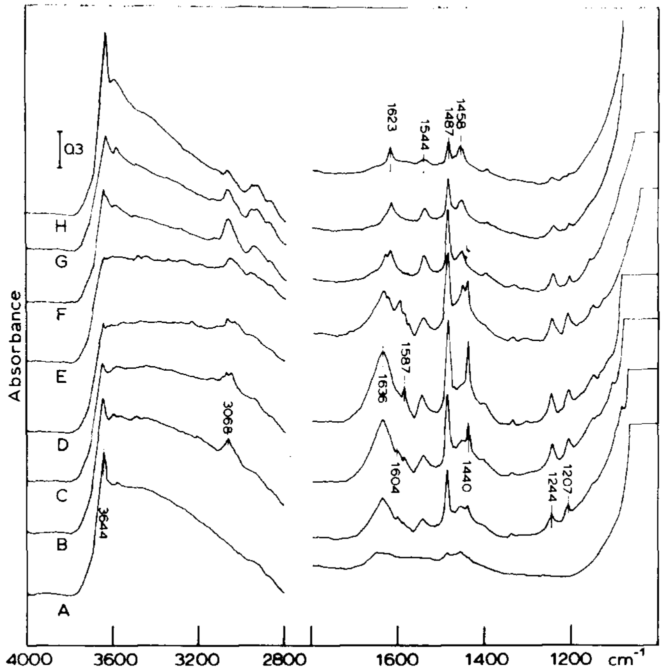

Fig. 5. Pyridine on NaH–GeX (29% exchanged). A, After outgassing at 200°C; B, adsorption of 1.8 μmol of pyridine; C, after adsorption of 3.2 μmol; D, after adsorption of 5 μmol of pyridine; E, outgassing at room temperature, 15 hr; F, evacuated at 100°C, 2.5 hr; G, evacuated at 140°C, 2 hr; H, evacuated at 180°C, 2 hr.

on a 29% NH_4-exchanged sample, outgassed for 15 hr at 200°C (spectrum A). This treatment is sufficient to provoke the decationation, i.e., the removal of NH_3 and the development of protonated sites, as inferred by the OH stretching bands at 3650 and 3590 cm^{-1}. The broad absorption between 3600 and 3200 cm^{-1} seems to be related to the exchange percentage in NH_4^+ and may originate from partial hydrolysis of the zeolite framework.

Successive adsorptions of pyridine (spectra B, C, and D) are accompanied by a progressive development of the bands at 1636, 1587, 1544, 1487, 1440, 1402, 1244, 1207, and 1160 cm^{-1}. The band at 1455 cm^{-1} does not seem to improve with increasing quantities of adsorbed pyridine. Compared to spectrum B of Fig. 4, the bands at 1587 and 1440 cm^{-1} are relatively less developed, whereas the bands at 1224, 1219, and 1148 cm^{-1} are not even observed; the band at 1636 cm^{-1} is appreciably more intense. Increasing amounts of pyridine adsorbed on the zeolite causes a decrease in intensity of the OH band at 3650 cm^{-1}.

After outgassing at room temperature (spectrum E), the band at 1636 cm^{-1} decreases in intensity, whereas the band at 1458 cm^{-1} markedly increases. Here again the bands at 1587 and 1440 cm^{-1} are the first to be removed when the disk is outgassed at increasing temperatures (spectra E–H). Partial desorption of pyridine at 100°C (F) completely removes the bands at 1587 and 1440 cm^{-1} and allows one to distinguish two bands at 1636 and 1623 cm^{-1}. At the same time the 3650-cm^{-1} band begins to appear. After outgassing at 140°C (G), the band at 1636 cm^{-1} has completely disappeared, whereas all the other bands of pyridine decrease. Heating *in vacuo* at 180°C (H) restores the band at 3650 cm^{-1}.

Figure 6 contains the spectra of pyridine adsorbed on a Ca-exchanged germanic

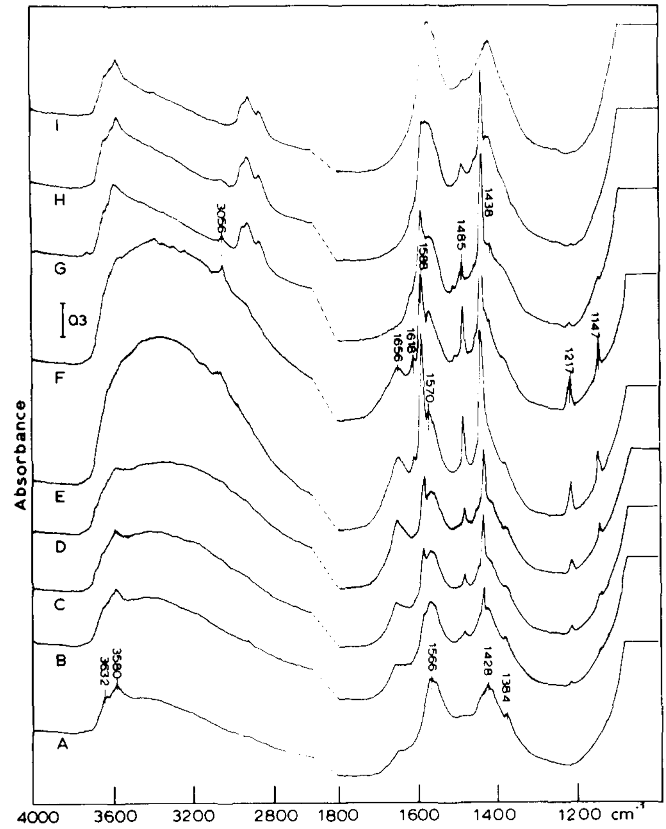

FIG. 6. Pyridine on NaCa-GeX (73% exchanged). A, After outgassing at 300°C, 11 hr; B, adsorption of 0.4 μmol of pyridine; C, 1.1 μmol of pyridine; D, 1.9 μmol of pyridine; E, 3.8 μmol of pyridine; F, desorption at room temperature, 1.5 hr; G, evacuated at 120°C, 1.5 hr; H, evacuated at 150°C, 1.5 hr; I, evacuated at 210°C, 15 hr.

near-faujasite (3.9 meq of Ca^{2+}/g). Spectrum A, obtained after evacuation at 300°C for 11 hr, shows several bands at 3632 and 3580 cm^{-1} in the OH stretching region, and at 1660 (shoulder), 1566, 1428, and 1384 cm^{-1} (shoulder). The last four bands are due to chemisorbed CO_2 species.

Upon adsorption of increasing quantities of pyridine (spectra B–E), bands develop at 3056, 1618, 1588, 1570, 1485, 1438, 1217, and 1148 cm^{-1}. All these bands were observed in the case of Na-GeX (Fig. 1). The two absorptions near 3400 and at 1656 cm^{-1} are due to traces of water. They are readily removed after outgassing at 120°C (G).

Outgassing at increasing temperatures (spectra F–I) shows a change similar to the one observed for Na-GeX; i.e., a progressive disappearance of all bands of pyridine. After outgassing at 210°C for 15 hr (I), the spectrum is slightly different from the initial one: The bands at 1566 and 1428 cm^{-1} of chemisorbed CO_2 are somewhat more intense.

DISCUSSION

Pyridine may be adsorbed on solid surfaces in four different states (*5*): physisorbed pyridine (or van der Waals interaction) (PyP), hydrogen-bonded pyridine (PyH), pyridine in interaction with a Lewis acid site (PyL), and pyridine in interaction with a Brønsted acid site (PyB). Infrared spectroscopy has been shown to be suitable for differentiating these different types of

TABLE 1

Wavenumber and Assignment of the Various ir Absorption Bands of Adsorbed Pyridine[a]

Type of interaction		Mode 19b	Mode 19a	Mode 8a	Mode 8b
van der Waals	PyP	1445–1450	1490 (vw)[b]	1579	—
H-bonded	PyH	id.	1490 (vw)	1595	—
Lewis site	PyL	1457	1490	1615–1625	1575 (vw)
Brønsted site	PyB	1540	1490	1640	1620

[a] From Scokart *et al.* (*10*).

[b] vw = very weak.

interaction, following the presence of specific absorption bands.

Table 1 taken from Scokart *et al.* (*10*), lists the typical frequencies of the in-plane vibrations of adsorbed pyridine according to the type of interaction.

Pyridine on Na–GeX

By analogy with its nearest homolog, the silicic Na–X, the germanic sieve should not possess detectable acids sites (Lewis or Brønsted). The examination of the spectra of Figs. 1–3 does not reveal the bands characteristic of PyB (at 1540 cm^{-1}) or PyL (at 1457 cm^{-1}). Pyridine is adsorbed in the physisorbed state, as substantiated by the band at 1570 cm^{-1}, which progressively disappears upon thermal treatment under vacuum, and more rapidly than the band at 1592 cm^{-1}. A second species, pyridine coordinately bound to the Na ions, is responsible for the bands at 1440 cm^{-1}, 1490, 1590, and 1618 cm^{-1}. These attributions are in total agreement with those of Ward on Na–X and Na–Y (*16*) sieves. This author showed that the frequency of the band near 1440 cm^{-1} varied linearly with the electrostatic field of the exchanged cation within the series of the alkali cations. Due to the absence of OH stretching bands, it is unlikely that there are H-bonded pyridine species.

An interesting feature of the germanic sieves is that the strong Ge–O stretching band is displaced, because of the bathochromatic effect due to Ge, toward smaller wavenumbers (*13*) clearing up the spectral region between 1200 and 1000 cm^{-1}, inaccessible in the case of the silicic sieves. This has been shown to be useful, for instance, in the adsorption of NH_3 (*1*). In the present case, adsorbed pyridine develops four additional bands at 1220, 1152, 1066, and 1029 cm^{-1}, which, according to Corrsin *et al.* (*17*) correspond to the 9a, 15, 18a, and 12 fundamental vibrational modes, respectively. Since these bands are not removed after outgassing at temperatures lower than 230°C, they are indicative of pyridine relatively strongly held on the surface. Accordingly, they are attributed to pyridine in coordination with the exchangeable cations.

The influence of small quantities of adsorbed water on the acidity of silicic Na–X and Na–Y has been investigated by various authors. Upon adsorption of pyridine on those sieves, Ward (*18*) observed only the bands of coordinately bound pyridine. Subsequent addition of small amounts of water followed by evacuation at room temperature, was marked by absorption bands at 3694, 3550, 3340, and 1640 cm^{-1}. No band due to pyridinium ions was detected. Upon evacuation at 150°C, these bands were completely removed.

On Na–GeX, adsorption of traces of water present in the pyridine (undried pyridine) is accompanied by the progressive development of two bands at 3400 and at 1665 cm^{-1}, as shown in spectra B and C of Fig. 3. These absorption bands, attributed to the OH stretching and deformation vibrations of undissociated water, are completely removed upon evacuation at moderate temperature (spectrum F in Fig. 3). No band due to pyridinium ions is observed which is in agreement with the results of Ward (*18*).

In conclusion, the Na form of the germanic near-faujasite does not show acid sites detectable by ir spectroscopy: Na–GeX does not behave differently, in this matter, from the Na–X and Na–Y zeolites. However, this does not signify a total absence of acidity. Isomerization of *n*-butenes performed at 280°C on Na–GeX showed a conversion of approximately 3% after 3 hr of reaction.

The low conversion observed in the 1-butene isomerization reaction (*19*), can be accounted for, in agreement with Lombardo *et al.* (*20*), by some cation deficiency resulting from the washings.

Finally, it should also be pointed out that the elimination of adsorbed water occurring at lower temperatures when pyridine is present has also been observed for Na–X and Na–Y zeolites (*18, 21*).

Pyridine on NaH–GeX

The ir spectra of Figs. 4 and 5 show, in addition to the bands of pyridine weakly held on the surface (PyP and PyH), the band at 1440 cm^{-1} characteristic of pyridine coordinated to the Na ions, and especially the bands at 1540 cm^{-1} and at 1455 cm^{-1}, typical of pyridine in interaction with Brønsted sites (PyB) or with Lewis sites (PyL), respectively.

Pyridine coordinately bound to the cations is eliminated before PyB and PyL, as observed by the rapid decrease in intensity of the bands at 1590, 1440, 1219, and 1148 cm^{-1} in Fig. 5 and particularly in Fig. 6. In those figures, the band at 1487 contains a contribution of PyL (true Lewis sites and coordinated pyridine) and of PyB.

The band near 1636 cm^{-1} (Fig. 5), increasing with the amount of pyridine adsorbed, cannot be attributed to weakly held pyridine since it disappears after those at 1440 and 1587 cm^{-1}. Such a band has been observed in several studies (*7, 10, 18*) and assigned, as the band at 1540 cm^{-1}, to pyridinium ions. The anomalous intensity of this band with regard to the 1544 cm^{-1} absorption is not in favor of such an attribution. Upon adsorption of pyridine on montmorillonite, Farmer and Mortland (*22*) observed a band near 1640 cm^{-1}, which was attributed to hydrogen-bonded pyridine. Such a species could possibly account for the band at 1636 cm^{-1}. However, this does not rule out a possible interaction of pyridine with water molecules adsorbed in traces on the surface and could explain the spectral modification occurring between 3200 and 3600 cm^{-1}, as shown in spectra B–E of Fig. 5.

The absorption band at 1622 cm^{-1}, also observed on protonated silicic X and Y sieves (*18*), is assigned, as the one at 1455 cm^{-1}, to pyridine adsorbed on Lewis sites.

In the region between 1250 and 1150 cm^{-1} (Fig. 5), five bands are visible at 1224, 1219, 1205, 1160, and 1148 cm^{-1}. The bands at 1219 and 1148 cm^{-1}, observed in the case of Na–GeX, change in the same manner as those attributed to pyridine in interaction of the Na^+ cations. They do not appear when the proton content (Fig. 6) is higher. The three other bands at 1244, 1205, and 1160 cm^{-1}, not found for Na–GeX, behave upon thermal treatment similarly to the 1540-cm^{-1} band. Indeed, as shown in Fig. 5, the intensities of these bands increase when the outgassing temperature goes from 105 to 150°C. For this reason they are attributed to PyB.

Qualitatively, the data on the surface acidity of protonated germanium sieves are in good agreement with those obtained on the silicic homolog X and Y zeolites (*23–26*): Both Brønsted and Lewis sites are found on NaH–GeX.

As for the silicic sieves, the OH band at 3650 cm^{-1} is affected by the adsorption of pyridine, whereas the 3540-cm^{-1} band, less intense, is not perturbed. This analogy allows us to assign the high-frequency component to vibration of O_I–H groups in the large cages (*7*, *27–30*), and the low-frequency band to OH groups involving framework O_3 atoms (*30–32*), probably hidden within the sodalite units. Jacobs and Uytterhoeven (*33*) showed, however, that the low-frequency band was a superposition of different components, involving O_2, O_3, and O_4 framework atoms.

The major difference between protonated silicic and germanic sieves lies in the strength of the interaction between pyridine and the acid centers. PyB and PyL species are less stable in the germanic sieve, as inferred from the lower temperatures necessary to remove the base completely. Indeed, outgassing at 230°C suffices to desorb all pyridine present on NaH–GeX, whereas on NaH–Y, for instance, no change in the 1545-cm^{-1} band occurs at outgassing temperature lower than 300–350°C (*34*). According to Tanabe (*35*), the weaker interaction implies that the acid strength of the supercage OH groups (and of the tricoordinated aluminum atoms associated with the Lewis sites) is weaker in the germanic sieve than in H–X and, *a fortiori*, in H–Y.

That Lewis sites are formed on the germanic sieve at temperatures lower than those necessary for such sites to appear in the silicic zeolites is not surprising and should be related to the lower structural stability of the former sieve, i.e., easier dehydroxylation, due, at least partially, to its higher Al content. It is known for the faujasite-type zeolites that the higher the Si/Al ratio, the more stable is the lattice.

Pyridine on Ca–GeX

The absence of the bands characteristic of PyB at 1545, 1244, and 1205 cm^{-1} in the spectra of Fig. 6 indicates that the calcium-exchanged germanic sieve does not develop acid sites such as those observed in silicic Ca–X and Ca–Y sieves (*15*, *18*, *36*). X and Y zeolites exchanged with divalent and trivalent cations dissociate to a different extent the water molecules of their hydration shell depending upon the associated polarizing field of the cation. For each series, the smaller the ionic radius, the higher the field and the number of Brønsted sites created on the surface. For the silicic zeolites, Ward (*37*) found an inverse correlation between the aluminum content and the intensity of the band due to pyridine adsorbed on Brønsted acid sites. If the number of protonic sites was only governed by the quantity of Ca^{2+} present, one would have expected a higher concentration of Brønsted sites on Ca–X than on Ca–Y.

The reason given by Ward to explain why Ca–X behaves differently from Ca–Y is based on the distance between the negative charge centers, which is shorter in X than in Y zeolite. The idea is that because of the higher Al content in the zeolite, the negative charges lie closer together so that they can be satisfied by a simple M^{2+} ion. In Y zeolite, the negative centers are more distant and charge neutralization cannot be achieved by M^{2+} alone. The equilibrium, $M^{2+}(H_2O) \rightleftarrows (MOH)^+ + H^+$, is displaced toward the right and one out of every two charges would be neutralized by a $Ca(OH)^+$ species, the second by a proton.

In the germanic sieve the Al/Ge ratio is 1 and, according to this hypothesis, one Ca^{2+} would still more easily satisfy two adjacent negative centers. In consequence of this, water would be still less dissociated than in the Ca–X sieve. This agrees fairly well with the experimental results shown in Fig. 6, where traces of water, responsible for the bands near 3400 and at 1656 cm^{-1}, do not generate Brønsted sites, as otherwise a band at 1540 cm^{-1} due to pyridinium ions should be observed.

CONCLUSIONS

No detectable acidity was found on Na–GeX, as indeed could be expected from past observations made on the Na–X and Na–Y homologs. However, contrasting with Ca–X and Ca–Y, Ca-exchanged germanic faujasite does not chemisorb pyridine as pyridinium, at least in measurable amounts. This is due either to the fact that residual water molecules are less dissociated on the germanic sieve than on the silicic sieves, because of the higher Al content of the former zeolite, or that the protons responsible for the OH stretching bands are not acidic enough to interact with pyridine.

In the partially protonated form, both Lewis and Brønsted sites are present, but the weaker interaction of pyridine with those centers is a witness of their lower acidic strength.

Hence, the absence of strong acid centers on the germanium sieve is consistent with the lower activities and the absence of secondary polymerization reactions, i.e., higher selectivities, toward isopropanol dehydration and isomerization of *n*-butenes.

ACKNOWLEDGMENT

M.L.D. acknowledges I.R.S.I.A. for a Ph.D. grant.

REFERENCES

1. Lerot, L., Poncelet, G., Dubru, M. L., and Fripiat, J. J., *J. Catal.* **37**, 396 (1975).
2. Lerot, L., Poncelet, G. and Fripiat, J. J., *J. Solid State Chem.* 12, 283 (1975).
3. Dempsey, E., Kuhl, G. H., and Olson, D. A., *J. Phys. Chem.* **73**, 387 (1969).
4. Poncelet, G., Dubru, M. L., and Jacobs, P. A., *in* "Molecular Sieves II" (J. R. Katzer, Ed.), Amer. Chem. Soc. Symposium 40, p. 606, 1977.
5. Parry, E. P., *J. Catal.* **2**, 371 (1963).
6. Bielanski, A., and Dakta, J., *Bull. Acad. Polon. Sci.* **22**, 341 (1974).
7. Hughes, T. R., and White, H. M., *J. Phys. Chem.* **71**, 2192 (1967).
8. Pichat, P., Mathieu, M., and Imelik, B., *Bull. Soc. Chim. Fr.* **8**, 2611 (1969).
9. Jacobs, P. A., Theng, B. K. G., and Uytterhoeven, J. B., *J. Catal.* **26**, 191 (1972).
10. Scokart, P. O., Declerck, F. D., Sempels, R. E., and Rouxhet, P. G., *J. Chem. Soc. Faraday Trans. 1* **73**, 359 (1977).
11. Ward, J. W., *in* "Zeolite Chemistry and Catalysis," (Rabo, Ed.), Amer. Chem. Soc. 171, 1976.
12. Jacobs, P. A., "Carboniogenic Activity of Zeolites." Elsevier, Amsterdam, 1977.
13. Lerot, L., Poncelet, G., and Fripiat, J. J., *Mater. Res. Bull.* 9, 979 (1974).
14. Jacobs, P. A., Van Cauwelaert, F. H., Vansant, E. F., and Uytterhoeven, J. B., *Trans. Faraday Soc. 1* **69**, 1056 (1973).
15. Uytterhoeven, J. B., Christner, L. G., and Hall, W. K., *J. Phys. Chem.* **69**, 2117 (1965).
16. Ward, J. W. *J. Colloid Interface Sci.* **28**, 269 (1968).
17. Corrsin, L., Fax, B. J., and Lord, R. C., *J. Chem. Phys.* **21**, 1170 (1953).
18. Ward, J. W., *J. Catal.* **11**, 238 (1968).
19. Watanabe, Y., and Habgood, H. W., *J. Phys. Chem.* **72**, 3066 (1968); Poncelet, G., and Dubru, M. L., unpublished results.
20. Lombardo, E. A., Sill, G. A., and Hall, K. W., *J. Catal.* **22**, 54 (1971).
21. Bertsch, L., and Habgood, H. W., *J. Phys. Chem.* **67**, 1621 (1963).
22. Farmer, V. C., and Mortland, M. M., *J. Chem. Soc. A*, 344 (1966).
23. Liengme, B. V., and Hall, W. K., *Trans. Faraday Soc.* **62**, 3229 (1966).
24. Ward, J. W., *J. Catal.* 9, 225 (1967).
25. Bielanski, A., and Dakta, J., *J. Catal.* **32**, 183 (1974).
26. Jacobs, P. A., and Heylen, C. F., *J. Catal.* **34**, 267 (1974).
27. Olson, D. H., and Dempsey, E., *J. Catal.* **13**, 221 (1969).
28. Uytterhoeven, J. B., Jacobs, P., Makay, K., and Schoonheydt, R., *J. Phys. Chem.* **72**, 1768 (1968).
29. Ward, J. W., *Advan. Chem.* **101**, 380 (1971).
30. Ward, J., and Hansford, R. C., *J. Catal.* **13**, 364 (1969).
31. Ward, J., *J. Phys. Chem.* **72**, 4211 (1968).
32. Ward, J., *J. Phys. Chem.* **73**, 2086 (1969).
33. Jacobs, P. A., and Uytterhoeven J. B., *Trans. Faraday Soc.* **69**, 359 (1973).
34. Bielanski, A., and Dakta, J. *J. Catal.* **37**, 383 (1975).
35. Tanabe, K., "Solid Acids and Bases," p. 10. Academic Press, New York, 1970.
36. Ward, J., *J. Catal.* **10**, 34 (1968).
37. Ward, J., *J. Catal.* **17**, 355 (1970).