JOURNAL OF CATALYSIS **139**, 81–92 (1993)

Quantitative Measurement by Infrared Spectroscopy of the Protonic Acidity of H-SAPO-37 and HY Using Benzene as a Probe

BAO LIAN SU[1] AND DENISE BARTHOMEUF

Laboratoire de Réactivité de Surface et Structure, URA 1106, CNRS, Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cédex 05, France

Received October 31, 1991; revised April 13, 1992

Infrared spectroscopy is used to characterize the hydroxyls of H-SAPO-37 and of highly exchanged HY and their interaction with benzene. A small number of hydroxyls still exists in H-SAPO-37 after pretreatment at 1173 K. This reflects a substantially higher thermal stability than in HY. The total number of protonic sites in H-SAPO-37 being less than in HY, there is enough space for benzene molecules in the supercage so that each proton (initially present or attracted into this cage) can interact with the aromatic molecule. It follows that the hydroxyls in the sodalite cage of H-SAPO-37 (3573 cm^{-1} band) almost disappear upon benzene adsorption, while in HY only a fraction of such hydroxyls can be attracted to the supercage and interact with benzene. The amount of molecules of benzene involved in this interaction is obtained from the study of the changes of the absorbance of the CH out-of-plane vibrations with benzene loading. This number greatly decreases as the pretreatment temperature of H-SAPO-37 is increased to 1173 K. The acid strength is followed by the shift $\Delta\nu_{OH}$ of the hydroxyls upon their interaction with benzene and by the amount of benzene remaining adsorbed at increasing pretreatment temperatures (C–C band at 1479 cm^{-1}). This shows that H-SAPO-37 has stronger protonic sites than HY and that heating above 973 K transforms some sites into stronger ones.

INTRODUCTION

The spectroscopic study of the adsorption of benzene on zeolites is a way to characterize precisely the interaction of the molecule with the adsorption sites at a molecular level. In faujasite (*1–6*) or Beta (*7*) zeolites exchanged with alkali ions two main adsorption sites have been shown to exist. The aromatic molecule can sit on cations through an interaction between the π electrons of the ring and the cations acting as Lewis-acid sites. A second, independent, site is the 12-ring window where the aromatic can be adsorbed with the CH weakly interacting with the framework oxygen. Proofs of these locations were obtained using various techniques such as NMR (*1*), neutron diffraction (*2, 3*), infrared spectroscopy (*4–8*), or theoretical calculations (*9*). The parameters governing the adsorption on the one site or the other were found to be, for a given zeolite structure such as for instance faujasite, the Lewis acidity of the cation and the basicity of the oxygen (*5, 6*). For KL zeolite at an average loading level of 1 molecule per unit cell (*10*) or up to 3 (*11*), the benzene molecule interacts mainly with the cations, as seen by neutron diffraction (*10*) or infrared spectroscopy (*11*). All these results suggest a specific molecular recognition between the adsorbate and the adsorption sites.

In the case of hydroxylated oxides (*12*) and specifically for protonic zeolites (*13, 14*) an interaction between the protons of the hydroxyls and the π electrons of the benzene ring has been proposed to explain the disturbances of the infrared hydroxyl spectra. A high shift of ν_{OH} upon benzene adsorption is taken as a measure of a strong acidity

---

[1] On leave from the Research Institute of Petroleum Processing, Beijing, China.

0021-9517/93 $5.00

of the proton (*12*). The comparison of various zeolites is hence made possible not only with regards to the acid strength deduced from $\Delta\nu_{OH}$, but also in considering in detail the changes in the infrared spectra of the hydroxyls of the zeolite and of the C–H and C–C vibrations of benzene.

In this view SAPO-37, which has the faujasite structure, is a good example to test the influence on the interaction benzene/zeolite of the presence of phosphorus in the structure. The present work is devoted to a detailed comparison of the interaction benzene/zeolite in the case of HY and H-SAPO-37 using infrared spectroscopy.

EXPERIMENTAL

NaY provided by Union Carbide was exchanged extensively in order to obtain a highly protonic material. A weight of 2.5 g of zeolite was added to 30 ml of solution of NH_4NO_3 (10 wt%) heated at 368 K. The suspension was mixed for 3 h at 368 K. The hot mixture was filtered and washed with hot distilled water (333 K) in order to remove NO_3 ions. The full exchange procedure was repeated seven times. The material dried in an oven at 393 K has the formula $(NH_4)_{56.4}Na_{0.7}Y$. It was heated to 673 K at a rate of 100 K per hour in a flow of dry oxygen. After 6 h at 673 K in oxygen atmosphere, the sample was evacuated for 6 to 8 h at 673 K and gives HY. It was checked that the crystallinity of the sample kept in a dry atmosphere is comparable to that of the starting NH_4Y. A higher desorption temperature dehydroxylates the zeolite. SAPO-37 with the formula $Si_{0.12}Al_{0.50}P_{0.38}O_2$ was prepared as in example 43 of Ref. (*15*) using tetramethyl- and tetrapropylammonium hydroxides as templates. The wafer used for the infrared study was treated in situ in the infrared cell, as for HY, up to 873 K. It was checked that after the evacuation at 873 K the template was fully removed and the H-SAPO-37 obtained was highly crystalline.

The adsorption of benzene was carried out on self-supported wafers (around 15 mg of hydrated zeolite, 18 mm in diameter) as described in Refs. (*5–7*). It was possible to adsorb on the samples increasing and known amounts of benzene step by step. The infrared measurements were carried out on self-supported wafers using a Perkin–Elmer 1750 Infrared Fourier Transform spectrometer equipped with a Data Station 1700. The relative absorbance Ar of the infrared bands was expressed as in Ref. (*6*),

$$\mathrm{Ar} = k\frac{M}{m}\int_{\text{bands}} A(\nu)d\nu, \qquad (1)$$

with M the weight of N unit cells of zeolite, m the weight of the wafer, and k a coefficient equal to 2.95×10^{-7} (*6*). The error bars on Ar in the figures were determined experimentally from a large number of experiments (*6*). All the spectra and results presented are related to the same number of unit cells of faujasite structure, i.e., that contained in 11 mg of HY heated at 1273 K.

Successive heat-treatments of H-SAPO-37 in the range 873 to 1073 K were performed on the same wafer after each benzene study followed by the evacuation of benzene at a rate of 100 K per hour up to successively 973 K and 1073 K. The pretreatment at 1173 K was carried on a second wafer which was first used to repeat the study after a heating at 1073 K.

RESULTS AND DISCUSSION

A. Interaction of Benzene with OH Groups

Figure 1 depicts the spectra of HY and H-SAPO-37 with and without adsorbed benzene. The OH range (3300–3800 cm^{-1}) and for benzene the CH out-of-plane bending vibration domain (1800–2100 cm^{-1}) and the stretching C–C mode (1479 cm^{-1}) will be described in detail. The 3000–3100 cm^{-1} domain corresponds to combination of stretching C–H and bending and stretching C–C. It is complex to be analyzed and will not be considered here.

As reported earlier, the hydroxyls of HY and H-SAPO-37 are very similar (*16, 17*).

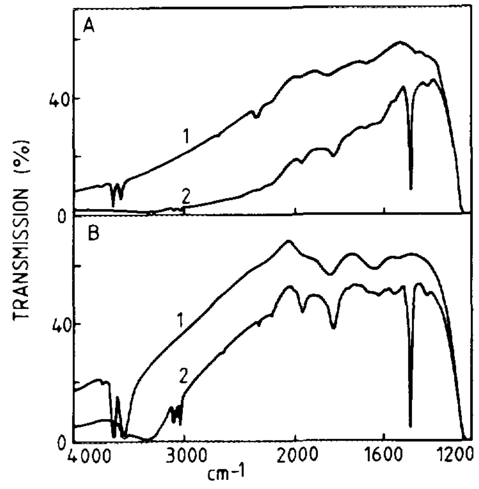

FIG. 1. Infrared spectra of H-SAPO-37 (A) and HY (B) without (1) or with (2) adsorbed benzene.

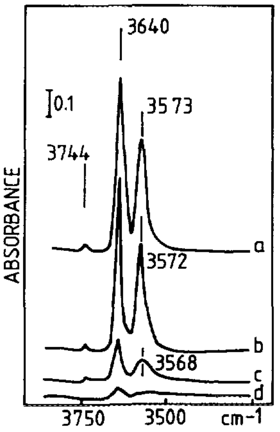

FIG. 3. Decrease in the hydroxyl absorbance of H-SAPO-37 after evacuation for 6–8 h at 873 K (a), 973 K (b), 1073 K (c), and 1173 K (d) (see text).

The adsorption of increasing amounts of benzene (Fig. 2) decreases both bands and generates as usual a broad OH band shifted to lower values upon its interaction with benzene. Figure 2A shows that in HY pretreated at 673 K mainly the 3644-cm^{-1} band (HF band corresponding to OH vibrating in the supercage) interacts with the aromatic. The 3550-cm^{-1} (*20*) band is only slightly decreased. This is usually explained by its location in the sodalite cage not accessible to benzene. The interaction of benzene with this OH in the sodalite is not strong enough to attract the protons into the supercage. However, in the case of H-SAPO-37 pretreated at 873 K (Fig. 2B) the two bands are simultaneously decreased and the 3573-cm^{-1} band almost disappears after adsorption of 4.3 molecules of benzene per supercage.

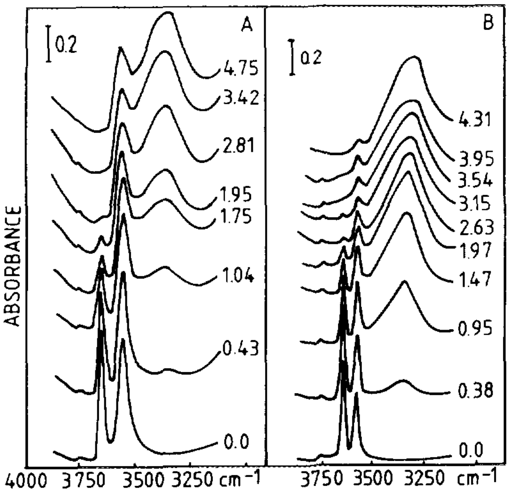

FIG. 2. Changes in the infrared absorbance of the hydroxyls of HY (A) and H-SAPO-37 (B) upon the adsorption of increasing amounts of benzene (in molecules per supercage) and pretreatments at 673 K for HY and 873 K for H-SAPO-37.

It was previously observed that heating H-SAPO-37 to 1173 K improves its catalytic properties (*18*) and that Brønsted acidity still exists after such a pretreatment (*17*). In order to better understand these properties the interaction of benzene with H-SAPO-37 evacuated up to 1173 K has been carried out. Figure 3 shows that even after evacuation at 1173 K some OH groups are still present in H-SAPO-37. The adsorption of increasing amounts of benzene on the materials evacuated at 973 and 1073 K gives results similar to that in Fig. 2B, that is to say, the 3640-cm^{-1} band disappears and the 3573-cm^{-1} band is greatly reduced at large benzene coverage. The small amount of hydroxyls

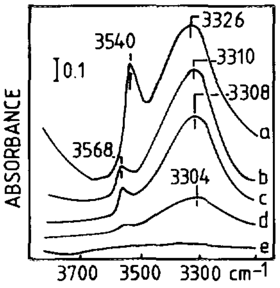

FIG. 4. Hydroxyl domain after saturation with benzene for HY and H-SAPO-37. The pretreatment temperatures and the amounts of benzene adsorbed in molecules per supercage are: (a) HY, 673 K, 4.75 m/s.c.; (b,c,d,e) H-SAPO-37; (b) 873 K, 4.31 m/s.c.; (c) 973 K, 4.56 m/s.c.; (d) 1073 K, 3.31 m/s.c.; and (e) 1173 K, 1.81 m/s.c.

present after the pretreatment at 1173 K is not high enough to be detected after its interaction with benzene. Figure 4 sums up the results for the shift of the hydroxyls in the five samples studied at saturation of the OH with benzene (see Section B). The $\Delta\nu_{OH}$ which can be calculated from the spectra of Figs. 3 and 4 are 318 ± 3 cm^{-1} for HY and 330 ± 3, 332 ± 3, and 336 ± 3 cm^{-1} for H-SAPO-37 pretreated at 873, 973, and 1073 K, respectively. These results suggest that the protons have a stronger acid strength in H-SAPO-37 than in HY. In addition, the acid strength in H-SAPO-37 tends to increase as the pretreatment temperature goes up, as seen from the resulting higher shifts. This is confirmed by the curves of Fig. 5, which compare the shifts $\Delta\nu_{OH}$ as a function of the amount of benzene adsorbed. It shows that at any benzene coverage the shift of the hydroxyls is higher after the pretreatment of H-SAPO-37 at 1073 K. Such an increase in acid strength was already suggested (*18*) in order to explain the rise in catalytic properties with the pretreatment temperature. It will be again considered later in this paper.

B. Benzene Disturbances and Amounts Adsorbed

The interaction of an adsorbate with a solid may be considered as *nonspecific* or *specific* (*12*). In the first case the interaction is determined mainly by dispersion forces. In *specific* molecular interaction the distribution of electrons in the adsorbate and on the adsorption centers plays an important role (*12*). Previous infrared studies of benzene adsorption on zeolites showed that the CH out-of-plane bending vibration is shifted, which indicates a strong polarization of the π-electron system, i.e., a specific interaction (*4–8*). It was possible to evaluate the amount of benzene involved in the most energetic part of this specific interaction by a quantitative study of the changes in absorbance of the CH out-of-plane infrared bands (*4–7*). Such an approach was applied to the case of the present samples.

Pretreatment at low temperature. Simultaneously with the changes upon benzene adsorption in the hydroxyl spectra reported in Fig. 2, the 1800–2100 cm^{-1} range shows an increase in the intensity of the CH out-of-plane bands (Fig. 6). The bands of the liquid are at 1815 cm^{-1} ($\nu_{10} + \nu_{17}$) and 1960 cm^{-1} ($\nu_5 + \nu_{17}$). Upon adsorption on HY pretreated at 673 K (Fig. 6A) or H-SAPO-37 pretreated at 873 K (Fig. 6B) the two bands are shifted to around 1830–1840 and 1975 cm^{-1}, the exact values depending on the loading. They are reported as an example in Fig. 7 for HY. These shifts are assigned to the interaction of the zeolitic protons with the π-bond system of benzene which modifies the CH vibration (*12*).

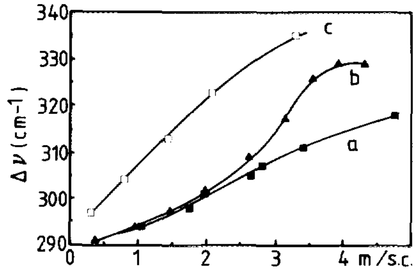

FIG. 5. Shifts of the high frequency OH band as a function of the amount of benzene adsorbed. (a) HY, (b) H-SAPO-37 pretreated at 873 K, and (c) H-SAPO-37 pretreated at 1073 K.

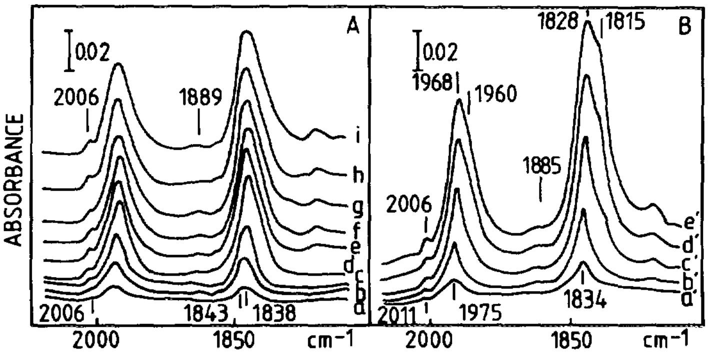

FIG. 6. Changes in the absorbance of the CH out-of-plane vibration as a function of the amount of benzene adsorbed on HY pretreated at 673 K (A) or H-SAPO-37 pretreated at 873 K (B). In molecules per supercage, (a) 0.43, (b) 1.04, (c) 1.75, (d) 2.81, (e) 3.43, (f) 4.03, (g) 4.75, (h) 5.75, (i) 7.21; (a') 0.38, (b') 0.95, (c') 1.97, (d') 2.95, (e') 4.13.

Considering first HY (Fig. 6A) it is seen that at low benzene coverage the (ν_{10} + ν_{17}) band is split into at least two components at 1838 and 1843 cm^{-1}. This might result from the presence of several types of protons. At high coverage or for the (ν_5 + ν_{17}) vibration the bands are broad and the splitting cannot be observed. A small pair of bands at 1889 and 2006 cm^{-1} might indicate the presence of few benzene molecules adsorbed in the 12-R window. The wavenumbers correspond to those, assigned this way, which are observed in the alkali cation forms of zeolites. In this case their intensity may be very high (*6*). Plotting the absorbance of the 1830–1840 and 1975 cm^{-1} bands expressed as in Eq. (1) and as described in detail in Refs. (*5*, *6*), as a function of the amount of benzene introduced in the cell gives Fig. 8. The absorbance reaches a constant value at an abscissa *P* around 4.5 ± 0.4 molecules of benzene per supercage (m/s.c.). No gas phase is detected in the cell by IR below the abscissa 3.7 m/s.c. Even at the point *P* almost all the benzene introduced in the cell is adsorbed, the relative pressure in the cell being less than 10^{-4}. A detailed study (*21*)

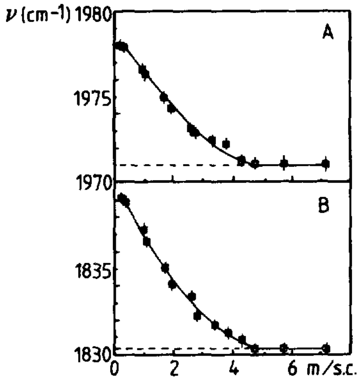

FIG. 7. Dependence of the wavenumber of the (ν_5 + ν_{17}) (A) and (ν_{10} + ν_{17}) (B) CH out-of-plane bands of benzene on the amount adsorbed on HY pretreated at 673 K.

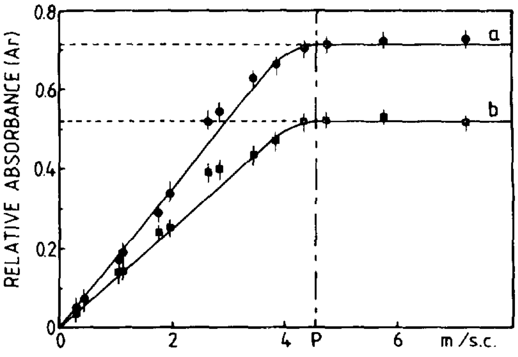

FIG. 8. Change in the relative absorbance of the (ν_{10} + ν_{17}) (a) and (ν_5 + ν_{17}) (b) bands of the CH out-of-plane vibration of benzene adsorbed in HY as a function of the amount of benzene adsorbed.

of the correlation for NaY between the curves as exemplified in Fig. 8 and the usual isotherm of benzene adsorption showed that the part below the abscissa *P* corresponds to the linear part of the isotherm. Above *P* the isotherm reaches progressively its maximum, the relative pressure increasing up to 0.5. This was also observed in this study, the isotherm of adsorption of benzene determined by infrared reaches a plateau for an amount of benzene of 4.8 m/s.c. for p/p_0 of 0.2 and higher. This corresponds to the adsorption capacity of faujasite (*5*, *22*). The point *P* may be considered as a pseudo-saturation of the zeolite, the amount adsorbed below this value being the more strongly held part of the benzene interacting in a specific way with the adsorbent (*21*). The value of 4.5 ± 0.4 for HY represents 94% of the total adsorption capacity of the zeolite. It has to be noted that the value of 4.5 m/s.c. is less than the theoretical number of protons calculated from the formula (7H$^+$/s.c.). There is not enough space in the cavities for a larger number of molecules and not every proton can interact with benzene. This might explain why the 3550-cm^{-1} band (Fig. 4) is not disappearing completely.

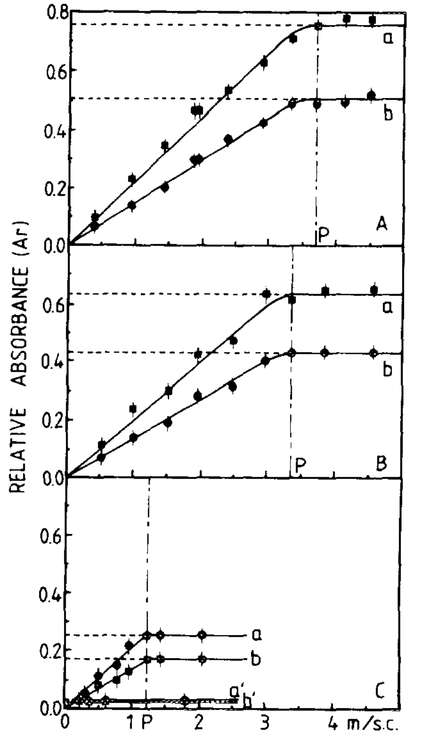

FIG. 9. Change in the relative absorbance of the (ν_{10} + ν_{17}) (a) and (ν_5 + ν_{17}) (b) bands of the CH out-of-plane vibration of benzene adsorbed in H-SAPO-37 pretreated at 873 K (A), 973 K (B), and 1073 K (C) as a function of the amount of benzene adsorbed. The curves (a') and (b') refer to the sample pretreated at 1173 K.

For H-SAPO-37 pretreated at 873 K (Fig. 6B) the general trend in the changes of the intensity of the CH out-of-plane vibration is the same as for HY. The wavenumbers of the $\nu_5 + \nu_{17}$ and $\nu_{10} + \nu_{17}$ bands are also similar. The presence of a small pair of bands at around 1885 and 2006 cm^{-1} is also noted and may characterize a very small number of benzene molecules in the 12-R windows. A main difference with HY is the appearance and the increase of a shoulder of the two bands at 1815 and 1960 cm^{-1} above loadings around 2 m/s.c. These wavenumbers characterize liquid benzene. One may suggest that above this amount some benzene is merely condensed in the cages giving a pseudo-liquid phase. This adsorption is typically nonspecific. In order to determine the amount of benzene adsorbed specifically (bands around 1830 and 1972 cm^{-1}) and nonspecifically (bands at 1815 and 1960 cm^{-1}), the bands of Fig. 6B were decomposed as described in Ref. (*6*). Figure 9A reports the changes in the relative absorbance evaluated from Eq. (1) of the specifically adsorbed benzene only, as a function of the amount of benzene introduced. As discussed for Fig. 8, the abscissa at the point *P* represents the amount of benzene strongly held by its interaction with the protons, i.e., around 3.7 ± 0.7 m/s.c. Above this point, the benzene nonspecifically adsorbed giving the 1815- and 1960-cm^{-1} bands and not counted in Fig. 9A may fill the cages.

It should be noted that the theoretical number of protons in H-SAPO-37, deduced from its silicon content, is 23 per unit cell, i.e., close to 3 per supercage. All the protons

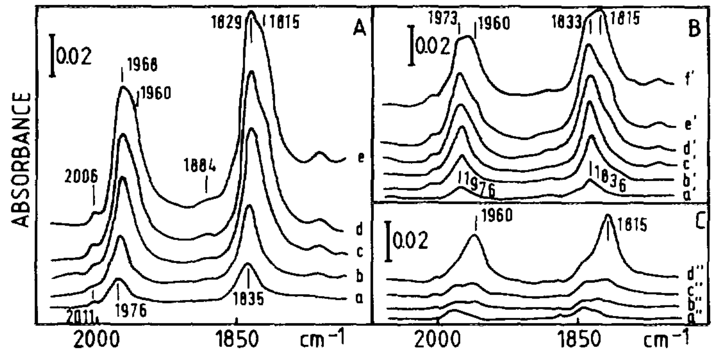

FIG. 10. Changes in the absorbance of the CH out-of-plane vibration of benzene as a function of the amount adsorbed in H-SAPO-37 pretreated at 973 K (A), 1073 K (B), 1173 K (C). In molecules per supercage, (a) 0.52, (b) 1.00, (c) 1.97, (d) 2.96, (e) 3.86; (a') 0.30, (b') 0.78, (c') 0.90, (d') 1.25, (e') 1.63, (f') 2.06; (a'') 0.22, (b'') 0.37, (c''), 0.61, (d'') 1.81.

might interact with benzene. By contrast with HY (56 H^+) where the supercage can contain less benzene molecules than there are protons, in the case of H-SAPO-37 (23 H^+) there is enough space in the large cavity to accommodate at least one benzene molecule per proton. All the protons are titrated.

Pretreatments at high temperatures. It is well known that HY dehydroxylates very rapidly above 673–723 K. This was checked in the present case and no study of benzene adsorption was performed on such dehydroxylated zeolites.

H-SAPO-37 is very stable upon heating (*23*) and the hydroxyls remain after high temperature pretreatments ((Ref. *17*) and Fig. 3). The spectra in the range 1800–2100 cm^{-1} for the samples pretreated at 973, 1073, and 1173 K are given in Fig. 10 as the amount of benzene adsorbed increases. For pretreatments at 973 and 1073 K (Figs. 10A and 10B) the curves have a shape similar to those of Fig. 6B for the 873 K case. As the temperature goes up, the absorbances decrease and the pseudo-liquid benzene (bands at 1815 and 1960 cm^{-1}) appears at lower loadings. After the 1173 K pretreatment there are still hydroxyls (Fig. 3). Their shift upon benzene adsorption could not be detected (Fig. 4). Nevertheless, the CH out-of-plane vibrations, even if they are weak, show clearly at low loading several weak bands in the range 1832–1843 and 1975 cm^{-1} (Fig. 10C). This indicates that the protons, even in small number, are strong enough so that the specific interaction with benzene can be detected. The bands at 1815 and 1960 cm^{-1} appear already for 0.37 m/s.c. adsorbed. This means that most of benzene which fills the zeolite cavities is merely condensed in a pseudo-liquid phase with no specific interaction with this H-SAPO-37 sample. As previously done for H-SAPO-37 pretreated at 873 K, the absorbances of the bands at 1830–1840 and 1975 cm^{-1} were calculated by decomposition of the spectra. The results are reported in Fig. 9 as a function of the amount of benzene introduced in the cell. The abscissa of the point *P* corresponding to benzene strongly held by its interaction with the protons decreases as the pretreatment temperature goes up. As previously in the case of HY the relative pressure in the cell is less than 10^{-4} at the point *P*. Figure 11 reports the abscissae at point *P*. They give access to the number of benzene molecules interacting with protons. Since as said above there is room enough in the cavities for having one aromatic molecule interacting with one proton in H-SAPO-37, this is also the number of protons after pretreatment at increasing temperatures. The curve of Fig. 11 is quite similar to the one obtained for other H-SAPO-37 materials studied by

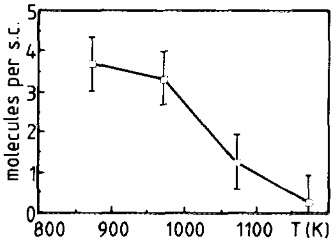

FIG. 11. Dependence of the abcissa of the point P (Fig. 9) on the pretreatment temperature of H-SAPO-37.

pyridine adsorption (*18*). The acidity of solids is usually evaluated by the changes in the absorbance of the pyridinium ion as a function of the pretreatment temperature. This gives a curve with a shape similar to that of Fig. 11 for H-SAPO-37 (*18*). Nevertheless, in the case of pyridine study the time-consuming procedure needed to have quantitative information on the number of sites after each pretreatment is usually not carried out, since it requires the determination of extinction coefficients. In the present benzene adsorption study, the amount of aromatic interacting with protons is obtained at the point *P* in Fig. 9 when the relative absorbance reaches a plateau as a function of amount adsorbed. It is not necessary to determine the extinction coefficient and Fig. 11 represents the number of protons which exist and interact with benzene after each pretreatment. The point *P* method used gives a quantitative measurement of protonic acidity.

The wavenumber of the CH out-of-plane bands does not give much information on the acid strength because a detailed study is difficult due to the broadness and the overlapping of bands (Figs. 6 and 10). In order to obtain more information, the strength of adsorption is considered by comparing samples at various desorption conditions.

C. Strength of Benzene/Proton Interaction

The evacuation of the wafer after the end of adsorption experiments was conducted for times ranging from 0.5 to 3 h at room temperature. In comparable experimental conditions, benzene which is adsorbed in $AlPO_4$-5 in the state of only the pseudo-liquid phase, nonspecifically interacting, is removed completely after 0.25 h evacuation (*24*). By contrast, it is necessary to heat to 383 K for NaY pretreated at 723 K to evacuate completely the benzene adsorbed (*24*).

For the HY sample pretreated at 673 K and for the H-SAPO-37 samples pretreated from 873 to 1173 K, the desorption of benzene for 0.5 h restores the hydroxyls within the accuracy of infrared measurements. Figure 12A reports the CH out-of-plane infrared range after 0.5 h evacuation at room temperature. There are still weak bands but they are broad and difficult to evaluate quantitatively. Taking into account the difference in scale between Figs. 6B and 10 and Fig. 12A, it can be estimated that at the most 0.1 m/s.c. of benzene remains adsorbed. This is less than 2 to 3% of the benzene molecules strongly interacting with protons in H-SAPO-37 pretreated at 873 or 973 K. A major point is the almost complete removal of benzene from the sample pretreated at 873 K by comparison with the pretreatment at 1173 K. A better accuracy is obtained by considering the 1479-cm^{-1} band (C–C stretching). It is sharper than the CH out-of-plane bands (Fig. 1). A disadvantage of this band is that it includes at high loading all the forms of benzene (interaction with the protons and with nonacidic OH, pseudo-liquid phase, capillary condensation). It follows that the intensity at full loading cannot be used as a reference. After evacuation (0.5 h or more) only the benzene interacting with the protons is still present since there are no bands at 1815 and 1960 cm^{-1} (Fig. 12A). Figure 12B gives the absorbance in the C–C region for the four H-SAPO-37 samples and HY after 0.5 h evacuation. It shows again for H-SAPO-37 a larger amount of benzene remaining adsorbed when the pretreatment temperature increases from 873 to 1173 K. The adsorbances reported in Fig.

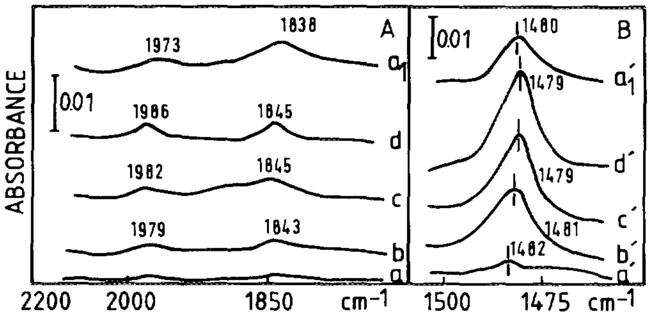

FIG. 12. Changes in the CH out-of-plane vibration (A) and C–C stretching ranges (B) after evacuation for 0.5 h at room temperature of benzene adsorbed on HY (a_1, a_1') or H-SAPO-37 (a–d and a′–d′) pretreated at 873 K (a, a′), 973 K (b, b′), 1073 K (c, c′), and 1173 K (d, d′).

13 show the same effect after 0.5 or 1 h, and Fig. 14 compares H-SAPO-37 with HY at longer evacuation times. The average order for the strength of adsorption of benzene is

H-SAPO-37 (873) < HY (673)
$\sim$ H-SAPO-37 (973) < H-SAPO-37 (1073)
$\ll$ H-SAPO-37 (1173).

Even a 3-h evacuation at room temperature does not remove all the benzene adsorbed on the H-SAPO-37 pretreated at 1173 K. These benzene molecules have to interact with strongly acidic protons. The results of Figs. 12–14 combined with those of Fig. 3 indicate that the hydroxyls, in a very small number after this treatment, are much stronger than after lower pretreatment temperatures. This is in agreement with the shift in OH described in Figs. 4 and 5 upon benzene adsorption. This shows that increasing the pretreatment temperature decreases the number of acidic protons but increases the strength of the remaining ones. This cannot be related to the appearance of extraframework species. Neither changes in the ^{27}Al or ^{31}P MAS NMR spectra are observed nor are new OH bands formed (*25*). The unit cell parameter does not decrease (*23*).

It may be observed in Fig. 12B that the wavenumber of the C–C vibration usually at 1479 cm^{-1} is shifted to 1482 and 1481 cm^{-1} in curves a′ and b′ (pretreatment of H-SAPO-37 at 873 and 973 K). Such a shift is related to a disturbance of the carbon ring breathing. In CsX this was ascribed to benzene molecules sitting in the 12-R window

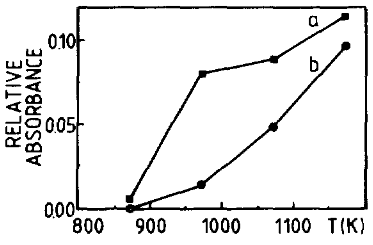

FIG. 13. Increase in the relative absorbance (peak area) of the 1479-cm^{-1} band (C–C vibration) as a function of the pretreatment temperature of H-SAPO-37 after evacuation of benzene for 0.5 h (a) and 1h (b) at room temperature.

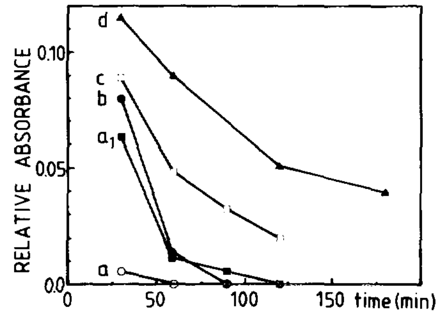

FIG. 14. Relative absorbance of peak area of the 1479-cm^{-1} band as a function of the evacuation time of benzene at room temperature for HY (a_1) and H-SAPO-37 pretreated at 873 K (a), 973 K (b), 1073 K (c), and 1173 K (d).

(*6*). As stated in Section B some aromatic molecules may be located in this site. They might be detected at very low loading by the shift of the C–C vibration mode but would give a broad CH out-of-plane peak in Fig. 12A, not observable.

D. General Discussion

H-SAPO-37 acid strength. It is well recognized that SAPOs have medium mean acid strengths. With SAPO-37 the major part of the acidity has this medium strength (*17, 19, 25, 26*). It was already proposed that a small number of sites have a strong acidity and that these strong sites may exist after pretreatment up to 1173 K (*17, 19*). The present study gives in addition information on the number and strength of sites of the protonic type. A comparison with HY shows that the hydroxyls in H-SAPO-37 are considerably more thermally stable. The dehydroxylation of H-SAPO-37 starts after 973 K and is not completed at 1173 K, while in the present HY the pretreatment at 773 K removes a large part of hydroxyls, none of them being seen above 823 K. The $\Delta\nu_{OH}$ upon benzene adsorption shows that in addition there are stronger protonic sites in H-SAPO-37 than in HY pretreated at 673 K. The total number of protons decreases as the pretreatment temperature increases. Nevertheless, the increase in the absorbance of the C–C vibration band (1479 cm^{-1}) indicates that the strong sites existing after pretreatment at 1173 K (*17, 19*) in H-SAPO-37 are protons and that they arise from the transformation of weaker sites into strong ones. The accuracy on the number of these strong sites is not very good (Fig. 9C, curves a′, b′). Out of an approximate number of 0.2 H^+/s.c. (Fig. 9C), Fig. 12 suggests that around 0.1 H^+/s.c. are strong, i.e., about 50%.

Considering the environment of sites, the present results suggest the following. First, the phosphorus atoms present in the framework as second neighbours of the Si atoms which generate acidity (*30*) reinforce the thermal stability of hydroxyls. Secondly, the acid strength may be explained by the environment of SiO_4. The sites with medium strength result from the presence of SiO_4 surrounded by four AlO_4 tetrahedra (Si(4 Al) sites). Such arrangements were shown to exist by ^{29}Si MAS NMR (*27–30*). Silicon islands in the framework generate other silicon environments (*28–30*). The Si *n*(Al) sites formed, with $n < 4$ at the border of the Si islands, may create strong acid sites in the same way as in faujasites (*28*). This may explain the presence of some strong sites. The increase in their strength, upon heating the H-SAPO-37, is seen from the present benzene adsorption study. Explanations may be proposed to account for this rise. It cannot be related to the formation of extraframework species which were not detected (*25*). It might result from an interaction between protons and Lewis sites whose number increases at higher pretreatment temperatures (*17, 25*). There might also be changes in the distribution of atoms in the framework upon heating. This point is presently under study.

Benzene as a probe to study acidity (amount and strength). General comments which can be made on the use of benzene to study the protonic acidity of zeolites are related to the information which can be deduced from the wavenumber shift of OH groups, and from the wavenumber and the absorbance of the CH out-of-plane vibration ($\nu_5 + \nu_{17}$ and $\nu_{10} + \nu_{17}$) and of the C–C stretching (ν_{19}, 1479 cm^{-1}) band.

Considering first the acid strength, the shift of wavenumber between the starting OH groups and the ones disturbed by their interaction with benzene gives good information. Nevertheless, since the shifted OH band is very broad and is the envelope of several hydroxyls, the location of its maximum may be affected by the proportion of acid sites of different strengths. If the strong sites are very strong their influence may become the most important in the $\Delta\nu_{OH}$ value. This occurs in H-SAPO-37, where a small number of strong sites may hide the influence of a large number of sites with medium strength. More specific to the strong sites only is the study of the CH out-of-plane and of the C–C vibration absorbance peaks which remain after evacuation of benzene at increasing times (Figs. 12–14). In the last case only the very strongly held benzene molecules are involved.

Information can be obtained on the amount of acid sites by studying the changes in the absorbance of the CH out-of-plane vibration as a function of benzene loading. It is possible to titrate the acidic protons which held benzene strongly (point P in Figs. 8, 9). It involves all the protons available with strong, medium or weak acidity but not the nonacidic OH groups.

Adsorbate–adsorbent interaction. A third piece of information given by the study of benzene adsorption concerns specifically the interaction proton/benzene. It is accepted that the protons of the hydroxyls interact through a hydrogen bond with the π cloud of the aromatic molecule (*12*). The present results show that this implies even at room temperature a change in the CH out-of-plane vibration, the wavenumber being shifted to high values at any loading. This indicates that even in the absence of any benzene–benzene interaction not expected to occur at low benzene coverage there is a disturbance of the benzene molecule. One may expect that other molecules with π electrons (olefins . . .) may be disturbed, even at low loading and at room temperature by their interaction with the protons. This would be an early step of the activation of molecules in catalysis. It is also observed for amounts of benzene adsorbed less or equal to 1 m/s.c. that benzene interacts with different protonic sites in HY (Fig. 6A) or H-SAPO-37 (Fig. 10C). At high loadings the information is lost in broad overlapping bands.

E. Conclusion

The detailed study of the protonic acidity of zeolites using benzene as a probe gives information on the acid strength and acid site number. It is very useful at small amounts of benzene adsorbed showing the disturbance of the aromatic molecule upon its interaction with the stronger sites of the zeolite. This approach clearly shows that the dehydroxylation of H-SAPO-37 is very different from that of HY. The heating above 973 K involves the transformation of some sites into centers of stronger protonic acidity. This unusual behaviour, related to the presence of P in the crystalline structure of faujasite, requires further studies.

ACKNOWLEDGMENTS

The authors thank Drs. D. Delafosse, M. Briend, and A. de Mallmann for very interesting discussions, and Drs. M. Briend and A. Morvan for the gift of the SAPO-37 and HY samples, respectively.

REFERENCES

1. Lechert, H., and Wittern, K. P., *Ber. Bunsenges. Phys. Chem.* **82,** 1054 (1978).

2. Fitch, A. N., Jobic, H., and Renouprez, A. J., *J. Chem. Soc., Chem. Commun.*, 284 (1985).

3. Fitch, A. N., Jobic, H., and Renouprez, A. J., *J. Phys. Chem.* **90,** 1311 (1986).

4. de Mallmann, A., and Barthomeuf, D., *J. Chem. Soc., Chem. Commun.*, 476 (1986).

5. de Mallmann, A., and Barthomeuf, D., *in* "Proceedings, 7th International Zeolite Conference, p. 609. Kodansha/Elsevier, Tokyo, 1986.

6. de Mallmann, A., and Barthomeuf, D., *Zeolites* **8,** 292 (1988).

7. Dzwigaj, S., de Mallmann, A., and Barthomeuf, D., *J. Chem. Soc., Faraday Trans.* **86,** 431 (1990).

8. Coughlan, B., and Keane, M. A. *J. Chem. Soc. Faraday Trans.* **86,** 3961 (1990).

9. Demontis, P., Yashonath, S., and Klein, M. L., *J. Phys. Chem.* **93,** 5016 (1989).

10. Newsam, J. M., Silbernagel, B. G., Garcia, A. R., and Hulme, R., *J. Chem. Soc., Chem. Commun.* 664 (1987).

11. Su, Bao Lian, and Barthomeuf, D., to be published.

12. Kiselev, A. V., and Lygin, V. I., "Infrared Spectra of Surface Compounds" Wiley, New York, 1975.

13. Datka, J., *J. Chem. Soc. Faraday Trans. I* **77,** 511 (1981).

14. Jacobs, P. A., Martens, J. A., Weitkamp, J., and Beyer, H. K., *Faraday Discuss. Chem. Soc.* **72,** 353 (1981).

15. Lok, B. M., Messina, C. A., Patton, R. L., Gajek, R. T., Cannan, R. T., and Flanigen, E. M., U.S. Patent 4 440 871 (1984).

16. Flanigen, E. M., Patton, R. L., and Wilson, S. T., *in* "Innovation in Zeolite Materials Science" (P. J. Grobet *et al.*, Eds.), Studies in Surface Science and Catalysis, Vol. 37, p. 13. Elsevier, Amsterdam, 1988.

17. Dzwigaj, S., Briend, M., Shikholeslami, A., Peltre, M. J., and Barthomeuf, D., *Zeolites* **10,** 157 (1990).
18. Su, Bao Lian, Lamy, A., Dzwigaj, S., Briend, M., and Barthomeuf, D., *Appl. Catal.* **75,** 311 (1991).
19. Briend, M., Lamy, A., Dzwigaj, S., and Barthomeuf, D., *in* "Zeolite Chemistry and Catalysis" (P. A. Jacobs *et al.*, Eds.), Studies in Surface Science and Catalysis, Vol. 69, p. 313. Elsevier, Amsterdam, 1991.
20. Jacobs, P. A., and Mortier, W. J., *Zeolites* **2,** 226 (1982).
21. de Mallmann, A., and Barthomeuf, D., *J. Phys. Chem.* **93,** 5636 (1989).
22. Breck, D. W., "Zeolite Molecular Sieves," p. 603 and 614. Wiley, New York, 1974.
23. Briend, M., Shikholeslami, A., Peltre, M. J., Delafosse, D., and Barthomeuf, D., *J. Chem. Soc. Dalton Trans.* 1361 (1989).
24. de Mallmann, A., Dzwigaj, S., and Barthomeuf, D., *in* "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), Studies in Surface Science and Catalysis, Vol. 49B, p. 935. Elsevier, Amsterdam, 1989.
25. Briend, M., Peltre, M. J., Lamy, A., Man, P., and Barthomeuf, D., *J. Catal.*, 1992, in press.
26. Corma, A., Fornes, V., Franco, M. J., Mocholi, F. A., and Perez-Pariente, J., *in* "Fluid Catalytic Cracking. II "Concepts in Catalytic Design" (M. L. Ocelli, Ed.), Vol. 452, p. 79. A. C. S., Washington, DC, 1990.
27. Sierra de Saldarriaga, L., Saldarriaga, C., and Davis, M. E., J. Am. Chem. Soc. **109,** 2686 (1987).
28. Martens, J. A., Janssens, C., Grobet, P. J., Beyer, H. K., and Jacobs, P. A., *in* "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), Studies in Surface Science and Catalysis, Vol. 49A, p. 215. Elsevier, Amsterdam, 1989.
29. Maistriau, L., Dumont, N., Nagy, J. B., Gabelica, Z., and Derouane, E. G., *Zeolites* **10,** 243 (1990).
30. Man, P. P., Briend, M., Peltre, M. J., Lamy, A., Beaunier, P., and Barthomeuf, D., *Zeolites* **11,** 563 (1991).