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Amphiprotic Properties of OH Groups in Synthetic NaHY Zeolites

A. BIELAŃSKI AND J. DATKA

Department of Chemistry, Jagellonian University, 30-060 Kraków, Poland

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The ir spectra of basic (pyridine) and acidic molecules (formic, acetic and benzoic acids) adsorbed on dehydrated NaHY zeolites were studied. Adsorbed pyridine molecules were transformed into pyridinium ions by reaction with the zeolitic OH groups characterized by the absorption peak at 3660 cm^{-1} and also to some extent with those exhibiting the absorption peak at 3565 cm^{-1}. In the presence of acid molecules the same OH groups reacted with the formation of carboxylic anions and water molecules. The zeolitic OH groups behave therefore as Brønsted acid centers in the presence of basic molecules and as Brønsted basic centers in the presence of acid molecules. Similar amphiprotic properties were shown by OH groups in an amorphous silica-alumina cracking catalyst.

INTRODUCTION

The acidic properties of decationated synthetic zeolites and especially of those belonging to the faujasite group have been the object of numerous investigations in recent years. Infrared spectroscopy has been applied successfully for this purpose (*1*) and it has been proved that both Brønsted and Lewis acid sites are present in the dehydrated NaHY zeolites in amounts depending on the composition of the sample and its pretreatment. Brønsted acid centers are formed by hydroxyl groups of two kinds. OH groups for which the stretching frequency 3650 cm^{-1} is characteristic react easily with pyridine forming pyridinium ions. Ammonia and piperidine behave similarly and also react additionally with OH groups exhibiting a stretching frequency at 3550 cm^{-1}. Strong Lewis acid sites bonding coordinatively pyridine molecules are present in the samples calcined at temperatures high enough to produce partial dehydroxylation. It has also been pointed out that sodium ions retained in the zeolite most probably play the role of weak Lewis acid centers.

The basic properties of alumino-silicate catalysts in contrast with acidic ones have been investigated in only a few cases, e.g., (*2*, *3*) and until the present work no extensive studies of the basicity of synthetic zeolites were undertaken. The need for such studies to be carried out parallel to investigations of acidic properties follows from the fact that the possibility of coexistence of both acid and basic centers on the surface of such catalysts as alumina (*4*) or silica gel appropriately prepared (*5*, *6*) has been proved and bifunctional mechanisms of catalytic reactions involving both kinds of centers have been proposed (*7*). The aim of the present research was to investigate the basic properties of the decationated NaHY zeolites by studying the ir absorption spectra of adsorbed acid molecules. For the sake of comparison with the results of the other authors the spectra of pyridine adsorbed on the same series of the samples have also been studied.

EXPERIMENTAL METHODS

Materials

Samples of NaHY zeolite were obtained from a preparation of NaY zeolite (Al_2O_3:SiO_2 molar ratio 1:5.22) which was transformed into $NaNH_4Y$ zeolite by treating it with NH_4NO_3 solution at 80°C. The degree of cation exchange determined flamephotometrically was 70%. The $NaNH_4Y$ zeolite was pressed into thin discs (3–7 mg/cm^2). The samples were decomposed into NaHY zeolite *in situ* in the measuring cell following the procedure described below.

Acetic acid (glacial), was kept over $KMnO_4$ and then distilled. The intermediate fraction was dried over P_2O_5 and taken for further experiments.

Formic acid was treated with anhydrous $CuSO_4$ and simultaneously boiled under the reflux. The traces of water which might still remain were removed with dehydrated $CaSO_4$ (Drierite BDM). The liquid was then distilled and the intermediate fraction was collected for further experiments. Dehydrated acetic and formic acids were stored over conc H_2SO_4.

Pyridine was dehydrated with freshly calcined KOH pellets and distilled. The preparation was then stored over dehydrated NaA zeolite.

All reagents used including benzoic acid to which no preparatory treatment was applied, were of analytical grade.

Procedure

The pressed discs of $NaNH_4Y$ zeolite were inserted into a measuring cell with sodium chloride windows. The construction of the cell, the details of which are given elsewhere (*8*), enabled samples to be outgassed *in vacuo* to 10^{-5} Torr, heating the samples to 700°C, followed by controlled adsorption of adsorbate vapors and the registration of ir spectra at room and elevated temperature. A Carl Zeiss UR-10 W double beam infrared spectrophotometer was used for the investigations.

Fresh discs were outgassed *in vacuo* by heating them slowly (2.5 deg/min) to 420°C. The sample was kept at this temperature for 3 hr. After cooling to room temperature no peaks characteristic of NH_4^+ ion and especially no 1430 cm^{-1} bands could be detected, which proved that the transformation of $NaNH_4Y$ into NaHY zeolite was complete.

RESULTS

Adsorption of Pyridine

The dehydrated NaHY zeolite showed an ir spectrum with two characteristic OH stretching vibrations at 3565 and 3660 cm^{-1}. The sample showed the same behavior towards pyridine adsorbed at room and at elevated temperatures as the samples described earlier (*1*), i.e., the intensity of the 3660 cm^{-1} band decreased and characteristic vibrations of pyridinium ions appeared. After all 3660 cm^{-1} OH groups had reached the reaction of 3565 cm^{-1} OH groups with pyridine was also observed.

Adsorption of Acetic Acid

In the course of introductory experiments we recorded the ir spectrum of acetic acid in the vapor phase and also the spectrum of anhydrous sodium acetate (Nujol mull). It has been stated that within the spectral region 1400–1800 cm^{-1} in which zeolite shows good transparency the following bands of CH_3COOH appear: 1430, 1515, 1725 and 1780 cm^{-1}. The spectrum of sodium acetate in this region is less rich and shows two bands only, viz, 1460 and 1590 cm^{-1}. The most characteristic band in the spectrum of CH_3COOH is the 1725 cm^{-1} band, corresponding to the stretching vibrations of the $C{=}O$ group, and in the spectrum of acetate ion the band of the asymmetric stretching vibrations of the COO^- group at about 1590 cm^{-1}.

Figure 1b shows the ir spectrum recorded after adsorption of acetic acid vapor on dehydrated NaHY zeolite at room temperature. Bands at 1415, 1720 and 1750 cm^{-1} are due to the adsorbed molecules of acetic acid, bands at 1480 and 1600 cm^{-1} are attributed to adsorbed acetate ions and that at 1650 cm^{-1} to the deformation vibrations of adsorbed water molecules. The intensity of all these bands distinctly increased with increasing amount of adsorbed acid vapor. Simultaneously a decrease in the intensity of 3660 cm^{-1} band of OH zeolitic groups was observed. The intensity of the other OH group band, namely that at 3565 cm^{-1}, initially did not change at all. On adsorbing larger amounts

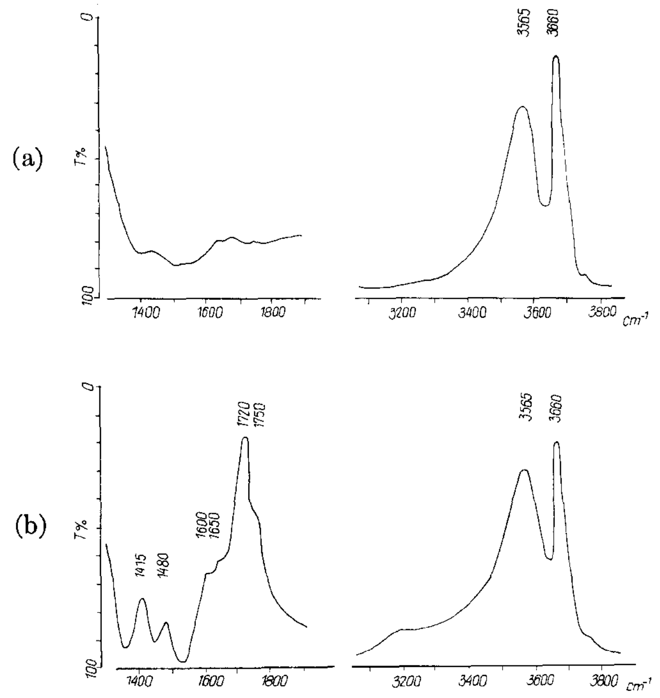

FIG. 1. Spectra of acetic acid adsorbed on dehydrated NaHY zeolite: (a) outgassed zeolite pellet; (b) zeolite pellet with adsorbed acetic acid, room temperature.

of CH_3COOH (about 50 μmole) a decrease in intensity of both OH bands was observed.

The above experiments show that at room temperature acetic acid is adsorbed mostly in the form of CH_3COOH molecules; however, a certain amount of it is transformed into acetate ions and water. Figure 2 illustrates the results obtained when the sample with adsorbed acetic acid is kept successively at room temperature, at 100, 200 and 350°C. Infrared spectra were registered 1 hr after the change of temperature. Raising the temperature to 100°C resulted in a distinct increase in intensity for the bands of acetate ions and water molecules which was accompanied by a decrease of the intensity of the CH_3COOH bands. No bands of acetic acid molecules were observed at 350°. At this temperature adsorption of a large amount of acetic acid caused a complete vanishing

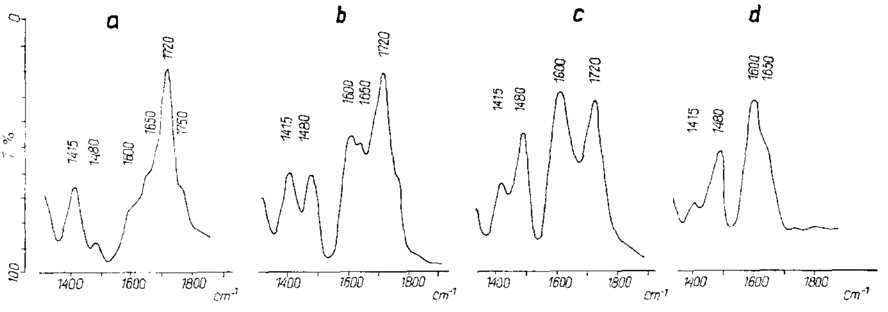

FIG. 2. Spectra of acetic acid adsorbed on NaHY zeolite registered at various temperatures: (a) Room temperature, (b) 100°C, (c) 200°C, (d) 350°C.

of both bands of zeolitic OH groups. Desorption at elevated temperatures caused the reduction of the bands of unreacted acetic acid and water; however, the intensity of the 1480 and 1600 cm^{-1} bands characteristic of acetate ions did not change. After desorption at 400°C only unchanged acetate bands were present in the spectrum.

No changes in the structure of the samples were detectable by X-rays after the treatment with acetic acid vapor (the investigated samples contained about 20% of unreacted OH groups).

All these experiments suggested very strongly that acetate ions are formed as the result of the reaction between zeolitic OH groups and CH_3COOH adsorbed molecules. It was thought that more information might be obtained in that respect by additional experiments with some other adsorbents. We therefore recorded the spectra of acetic acid adsorbed on dehydrated NaY zeolite which did not contain any OH groups, and also carried out similar experiments with an amorphous silica–alumina industrial cracking catalyst (Crosfield, 13% Al_2O_3, 87% SiO_2) and with amorphous silica (Aerosil).

The absorption spectrum of acetic acid adsorbed on a pellet of NaY zeolite (outgassed for 3 hr at 420°C) contained only the 1515, 1720 and 1750 cm^{-1} bands of adsorbed CH_3COOH molecules. No bands of acetate ion were registered. Desorption at 400°C resulted in complete disappearance of adsorbed acetic acid.

Figure 3a shows the spectrum of the silica–alumina catalyst outgassed at 400°C for 3 hr. A sharp OH band at 3757 cm^{-1} is then seen but no appreciable absorption between 1400 and 1800 cm^{-1}. Adsorption of pyridine at 150°C (Fig. 3b) is accompanied by the appearance of the 1545 cm^{-1} band characteristic of pyridinium ion and also of the 1453 cm^{-1} band of pyridine coordinatively bonded. Also the 1490 and 1620 cm^{-1} bands appearing in the spectra of pyridine adsorbed on both Brønsted and Lewis centers were observed. Simultaneously there was a decrease in the intensity of the OH band. Hence, both Brønsted and Lewis acid centers are present at the catalyst surface. Subsequent outgassing of the sample at 500°C resulted in the complete vanishing of the bands of both forms of adsorbed pyridine and the restoration of the OH 3757 cm^{-1} band to its initial height.

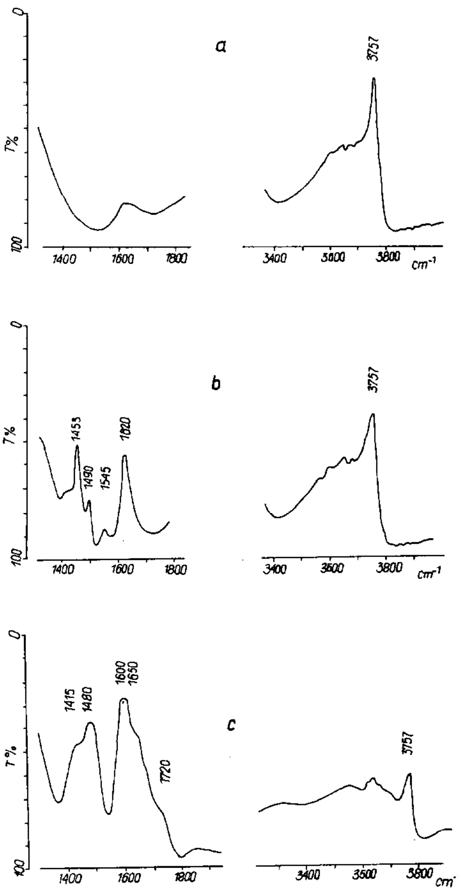

FIG. 3. Spectra of pyridine and acetic acid adsorbed on amorphous silica–alumina cracking catalyst: (a) outgassed pellet of the catalyst; (b) pyridine adsorbed at 150°C; (c) acetic acid adsorbed and spectrum recorded at room temperature.

As Fig. 3c shows, the spectrum of acetic acid recorded at room temperature soon after contacting the adsorbate with the adsorbent exhibits distinct bands at 1480 and 1600 cm^{-1}, corresponding to the acetate ion, as well as the less intense bands of CH_3COOH molecules at 1415 and 1720 cm^{-1} and the band of water molecules at 1650 cm^{-1}. Simultaneously the band of the alumino–silicate OH groups at 3757 cm^{-1}

markedly diminished. After 10 hr the latter band vanished completely. It is therefore seen that principally the behavior of the alumino–silica catalyst towards pyridine and acetic acid molecules is similar to the behavior of NaHY zeolite. It should be noted, however, that at room temperature the alumina–silica catalyst reacts more easily with CH_3COOH molecules than does NaHY zeolite.

Similar results were obtained by Uytterhoeven, Fripiat and Dockx (*3*) who investigated the spectra of acetic acid adsorbed on a sample of silica–alumina catalyst.

No adsorption of pyridine on Brønsted or Lewis acid centers was detected in the case of the outgassed Aerosil sample. On adsorbing acetic acid, only the bands of CH_3COOH molecules were observed at room or elevated temperatures. No bands of acetate ions appeared. The silica OH group band at 3750 cm^{-1} somewhat diminished in intensity after contacting the sample with acetic acid vapor, but simultaneously the overlap of a new band of lower frequency was observed which indicated the formation of hydrogen bonds between OH groups and CH_3COOH molecules. Outgassing the sample at 400° restored the initial spectrum of the sample.

Adsorption of Formic Acid

In the ir spectrum of formic acid (about 10 μmoles) adsorbed on NaHY zeolite at room temperature we observed the bands at 1385 and 1630 cm^{-1} characteristic of formate ions and the band of HCOOH molecules at 1720 cm^{-1} (Fig. 4a). A decrease in the intensity of the bands of zeolitic OH groups was simultaneously observed. The results are therefore very similar to those obtained with acetic acid.

As Fig. 4b and c show, an increase of temperature contributes to a decrease in the intensity of all bands corresponding to the molecules of formic acid as well as formate ions. No OH band intensities are then restored. At 200°C only a small band at 1635 cm^{-1} was observed. This band is not due to the formate ions because the other band of these ions at 1385 cm^{-1} vanished completely. It must be attributed to the bending vibrations of adsorbed water molecules. Formate ions when adsorbed are therefore less stable than the adsorbed acetate ions.

Outgassing the sample at 400°C after the experiments with formic acid resulted in the complete desorption of adsorbed species; also no bands of OH groups were registered. The sample was subsequently cooled to 150°C and a quantity of pyridine was adsorbed on it. After pumping at 400°C in order to remove loosely bonded pyridine (pyridine adsorbed physically and coordinated to weak Lewis acid centers such as Na^+ ions), the ir spectrum was recorded. As Fig. 4d shows, only a weak band at 1545 cm^{-1} characteristic of the pyridinium ion was present, thus showing that a small number of OH groups not detectable directly still remained. Strong bands, how-

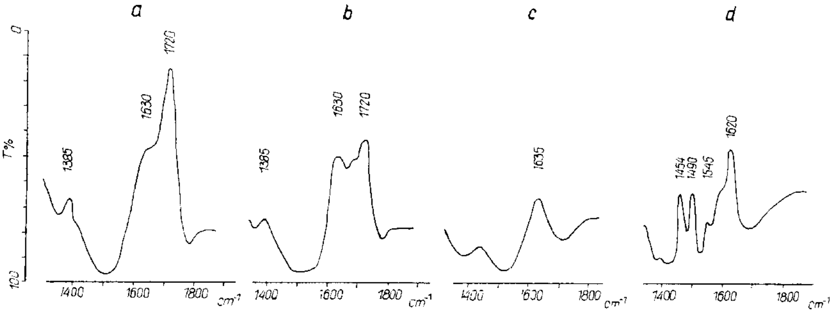

FIG. 4. Spectra of formic acid adsorbed on NaHY zeolite recorded at various temperatures: (a) room temperature, (b) 100°C, (c) 200°C, (d) pyridine adsorbed at 150°C, evacuated at 400°C. Spectrum recorded at 150°C.

ever, appeared at 1454, 1490 and 1620 cm^{-1} corresponding to the vibrations of pyridine coordinatively bonded. The treatment of the zeolite with formic acid therefore resulted in the formation of strong Lewis acid centers at the sites where acid molecules had reacted with OH groups.

In an additional series of experiments the saturated vapor of formic acid was introduced into the cell at 300°C and kept there for 1 hr. Neither bands of formic acid, formate ions nor of OH groups were observed after this period of time. The spectrum, however, contained a band due to bending vibrations of water at 1635 cm^{-1} and two bands at 2110 and 2160 cm^{-1} corresponding to the bands at 2120 and 2160 cm^{-1} observed by Angell and Schaffer (*10*) as the result of adsorption of CO on X and Y zeolites.

Adsorption of Benzoic Acid

Benzoic acid has a low vapor pressure at room temperature. Nevertheless, after several hours of contact with outgassed NaHY zeolite the ir spectrum of adsorbed benzoic acid could be registered. By comparing it with the spectra of pure benzoic acid and sodium benzoate we arrive at the conclusion that the bands at 1490, 1580 and 1700 cm^{-1} shown in Fig. 5a should be attributed to the unreacted benzoic acid molecules and weak bands at 1455 and 1605 cm^{-1} to benzoate ions. Increasing the temperature to 200° (Fig. 5b) resulted in some decrease in the intensity of the benzoic acid bands and increase in the intensity of the benzoate ion bands. During all these operations at room as well as elevated temperature the intensity of both bands corresponding to zeolite OH groups (3565 and 3660 cm^{-1}) gradually decreased. After 1 hr at 350°C the bands of benzoic acid disappeared almost completely due to desorption and condensation in the cold regions of the ir cell. The remaining bands of benzoate ions although somewhat diminished are now better resolved, as seen in Fig. 5c. The disappearance of the broad band at 1700 cm^{-1} enabled now the observation (at room temperature) of the band at 1630 cm^{-1} corresponding most probably to the bending vibration of adsorbed water molecules.

Discussion

In the ir spectrum of NaHY zeolite two OH bands at 3660 and 3565 cm^{-1} were observed in accordance with previous investigations (*1*). Both kinds of OH group are assumed to be hydroxyl groups in close proximity to aluminum atoms. They differ, however, in their environment and both show the properties of Brønsted acid centers when in contact with basic molecules such as piperidine, ammonia and also pyridine, the latter reacting preferentially with the 3660 cm^{-1} OH group. The same behavior was also observed in the case of our samples.

In the present investigations, however, it has been shown that the same 3660 and 3565 cm^{-1} OH groups in contact with organic acid molecules are also capable of

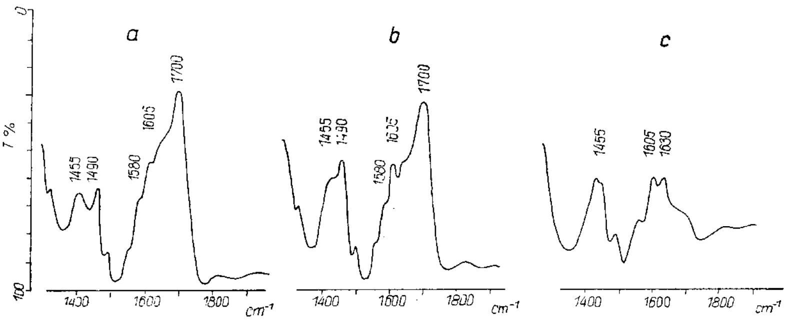

FIG. 5. Spectra of benzoic acid adsorbed on zeolite NaHY and recorded at various temperatures: (a) room temperature, (b) 200°C, (c) 350°C.

playing the role of Brønsted basic centers. On reacting with acid molecules they produce water and carboxylic anions:

$$\text{zeol.–OH} + \text{HOOC·R} \rightarrow \text{zeol.}^+ + \text{R·COO}^- + H_2O.$$

Both kinds of OH groups in zeolites therefore exhibit amphiprotic properties.

Similar properties of OH groups were also noted in the case of an amorphous silica–alumina catalyst. But they were not observed for OH groups in hydrated silica, which did not react either with pyridine or with acetic or formic acid. On the other hand, the hydroxyl Al–OH groups in alumina according to Fink (*9*) behave as Brønsted basic centers in contact with CH_3COOH and HCOOH vapors, but do not react with pyridine (pyridine reacts only with Lewis acid centers present at the surface of alumina).

It seems therefore that amphiprotic properties of surface OH groups appear only if they are localized in the vicinity of both Si and Al atoms and not the OH groups on the surface of silica or alumina. It may be noticed here that amphiprocity of surface OH groups has been observed by Primet, Pichat and Mathieu (*11*) also in the case of titanium dioxide.

At room temperature only a small fraction of adsorbed acid molecules reacts with OH groups. With increasing temperature the amount of reacted acid molecules also becomes larger. The complete transformation of formic acid molecules into formate ions was already observed at 200°C and that of acetic and benzoic acid at 350°C. These qualitative observations show certain differences in the behavior of the investigated acids. The acids also differ in the thermal stability of their anions. Adsorbed acetate ion is most stable in the sense that it remains in the sample even after outgassing at 400°C and only at this temperature slowly decomposes with the formation of products which turned the sample light brown. Formate ions decompose already at 200°C and it may be supposed that the decomposition of formic acid on NaHY zeolite proceeds through the formation of formate ions as intermediate. In such a case zeolitic OH groups would play the role of Brønsted basic centers in the course of a catalytic process.

ACKNOWLEDGMENT

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