INVESTIGATIONS ON THE ACIDITIES OF DIFFERENT TYPES OF ZEOLITES

By

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Different zeolites were characterized by means of X-ray diffraction, derivatography and infrared spectroscopy. The acidities of the zeolites were determined by pyridine adsorption. The literature data concerning the absorption coefficients of pyridine adsorbed on acidic sites are critically evaluated.

Introduction

The characterization of zeolite catalysts used for investigations of the mechanisms and kinetics of hydrocarbon transformation is indispensable, and includes (i) an estimation of the number and nature of potential active sites; (ii) determination of the temperature range of operation in which no essential structural changes occur in the catalysts.

Kinetic data, i.e. apparent rate constants and activa-

tion energies, usually obtained from kinetic experiments sup-
plemented with the predetermined physical properties of the
catalysts, may provide a promising data-set for the computer
optimization of kinetic models.

The present study deals with the acidities and partly
also with the thermal stabilities and crystallinities of the
zeolites used in adsorption, kinetic and spectroscopic meas-
urements with the aim of investigation of the kinetics and
mechanisms of the cracking of short-chain paraffins.

Derivatography, X-ray diffraction and ir spectroscopy
were used to acquire data for catalyst characterization.

Experimental

NH_4^+-zeolites were prepared from their sodium forms. In
order to obtain samples with different ammonium ion contents,
NaY (Linde) was ion-exchanged with NH_4Cl solutions of dif-
ferent concentrations for 12 h at 350 K.

NH_4^+-mordenite was obtained by ion-exchange of Na-mor-
denite (Norton) in 0.1 mol/dm^3 NH_4Cl solution at 350 K for
12 h (the procedure was repeated three times with fresh solu-
tions).

In the case of zeolite ZSM-5, the following procedure
was used. The starting material, the zeolite ZSM-5 "as
synthesized", was baked out at 770 K in flowing air for 12 h
in order to burn off the organic template. This raw material
was converted into its sodium form by repeated ion-exchange
in 0.1 mol/dm^3 NaCl solution at room temperature, and then
washed with water. NH_4^+-ion-exchange of NaZSM-5 was performed

at room temperature and repeated three times following the preparation procedure proposed by Dwyer [1].

After ion-exchange, the NH_4^+ forms of the zeolites were carefully washed with distilled water until the filtrate was Cl^--free, then dried and stored over saturated NH_4Cl solution to obtain samples with a standard water content.

The compositions of the samples were determined by neutron activation analysis (Y and mordenite) and atomic absorption spectroscopy (ZSM-5), and are given in Table I.

Table I

Unit cell compositions of the zeolites under study

Sample	Unit cell composition	Water content, m %
NaY	$Na_{58}Al_{58}Si_{134}O_{384}$	28
H1Y	$(NH_4)_5Na_{53}Al_{58}Si_{134}O_{384}$	+
H2Y	$(NH_4)_{32}Na_{26}Al_{58}Si_{134}O_{384}$	+
H3Y	$(NH_4)_{42}Al_{16}Al_{58}Si_{134}O_{384}$	+
NaM	$Na_{6.5}Al_{6.5}Si_{41.5}O_{96}$	12
HM	$(NH_4)_{6.3}Na_{0.2}Al_{6.5}Si_{41.5}O_{95}$	+
NaZSM-5	$Na_{1.08}Al_{1.08}Si_{94.9}O_{192}$	6
HNaZSM-5	$(NH_4)_{1.02}Na_{0.006}Al_{1.08}Si_{94.9}O_{192}$	+

+ The water content was not available for these samples.

Results and Discussion

Characterization of samples by X-ray and ir spectroscopy

To check the crystallinity of each catalyst sample, and its change under the conditions of preparation and activation, X-ray diffraction and ir spectroscopy (in the range of framework vibration, 400-1300 cm^{-1}) where used. X-ray diffraction analysis was carried out at ambient temperature, with a DRON-3 diffractometer. For the KBr pellet technique, a SPECORD-75 IR spectrophotometer was utilized. In each case, wafers of 1 m % zeolite in KBr were recorded vs. an empty KBr pellet.

Figure 1 shows a set of diffractograms selected to demonstrate the characteristic reflexions of the zeolites tested. No change in crystallinity due to ion-exchange was detected. In contrast, the removal of the organic template influenced the X-ray pattern of ZSM-5, as can be seen in Figure 1. The change in intensity of reflexions as a result of template removal is well known and has been discussed in the literature [2-7].

The ir spectra show obvious differences, depending on the structures of the zeolites used (see Figure 2). The frequencies observed are in good agreement with the literature data [8-12]; they are listed in Table II. According to Flanigen [13], absorptions at around 1100, 700 and 450 cm^{-1} are assigned to internal vibrations of the tetrahedra. The bands at 650-550 cm^{-1} are characteristic of the presence of double-rings of tetrahedra. Absorption in the range 1000-1200 cm^{-1} are due to external asymmetric motions.

The method of Coudurier [11], according to which the ratio of the absorbances of the bands at 650-550 and 480--440 cm^{-1} is a good measure of the crystalline fraction of
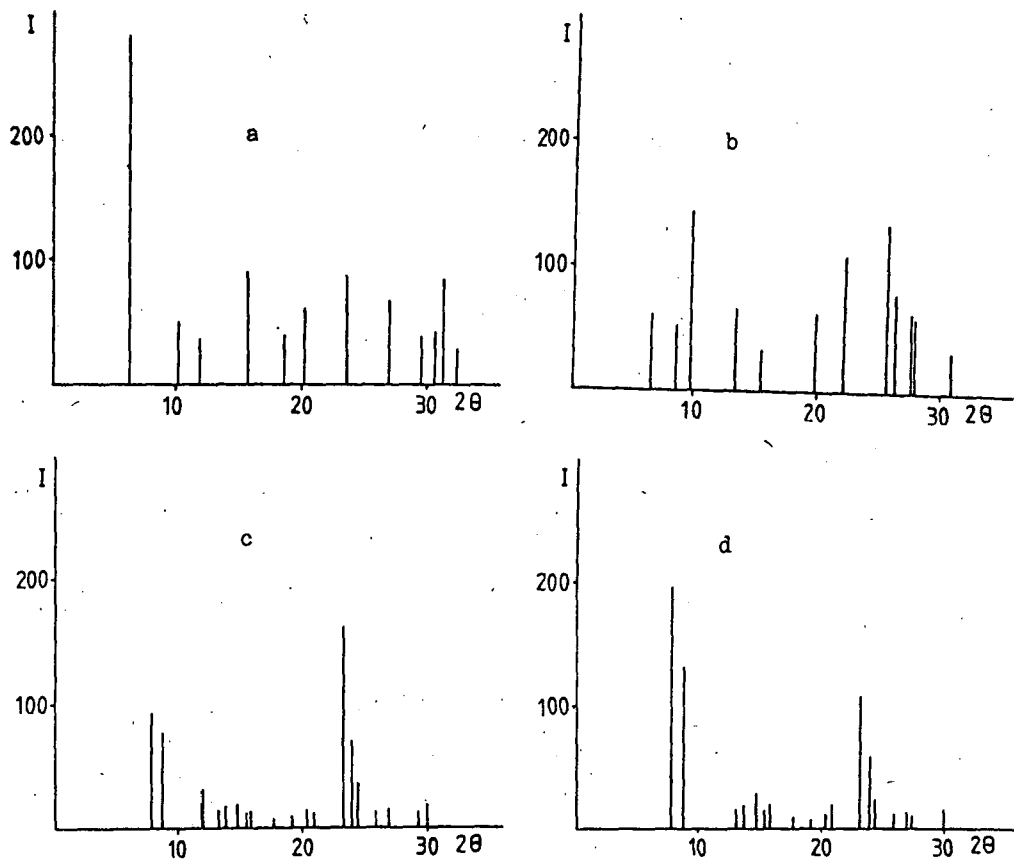

Figure 1.: X-ray diffractograms of zeolites tested:
    a/ NH_4NaY,   b/ NH_4Na-mordenite,
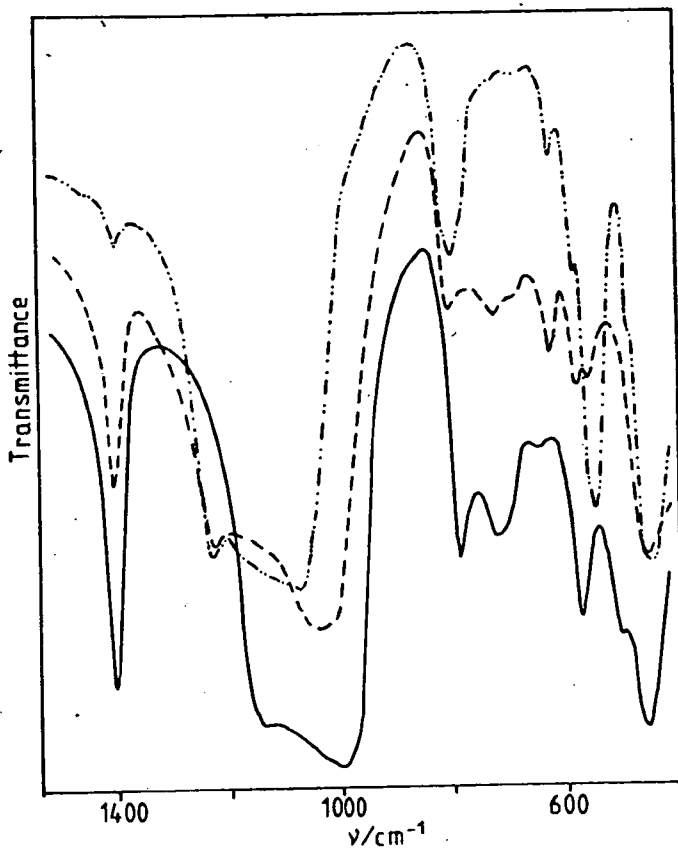   c/ ZSM-5 "as synthesized",   d/ NH_4ZSM-5

Figure 2.: Ir spectra of NH$_4$NaY (------), NH$_4$Na-mordenite
(- - - - -) and NH$_4$ZSM-5 (-..-..-) in the range
of framework vibration.

Table II

Observed bands in the range of framework vibrations

Zeolite	Frequencies, cm^{-1}							
NH$_4$NaY	460	505	575	640	720	785	980	1140
NH$_4$NaM	460	520	545	625	730	805	1005	1230
NH$_4$NaZSM5	450	546	585	626	680	800	1080	1230

a given zeolite, results in characteristic ratios of 0.24, 0.51 and 0.72 for the zeolites; these should be compared with the values we obtained: 0.19, 0.49 and 0.78 for mordenite, zeolite Y and ZSM-5, respectively.

Comparison of the ammonium contents of the samples obtained from their chemical analysis and those determined from the absorbance of the NH$_4^+$ band at 1400 cm^{-1} (0.67, 0.5 and C.04 for NH$_4$NaY, NH$_4$NaM and NH$_4$NaZSM-5, respectively) shows a good linear relationship.

Thermogravimetric investigations

Derivatographic experiments were performed with a DERIVATOGRAPH-Q instrument. Zeolites were placed on platinum plates. The thermograms were recorded in air at a heating rate of 5 K/min. Information obtained from these measurements can only be regarded as approximate, as the transformations taking place in zeolites under high-vacuum conditions (especially in the case of NH$_4^+$ forms) depend strongly on the experimental conditions, i.e. heating rate, atmosphere over the sample, thickness of the zeolite layer, etc. [14-19].

A typical derivatographic pattern of zeolite NH$_4$NaY is depicted in Figure 3. The TG curve shows three, not clearly
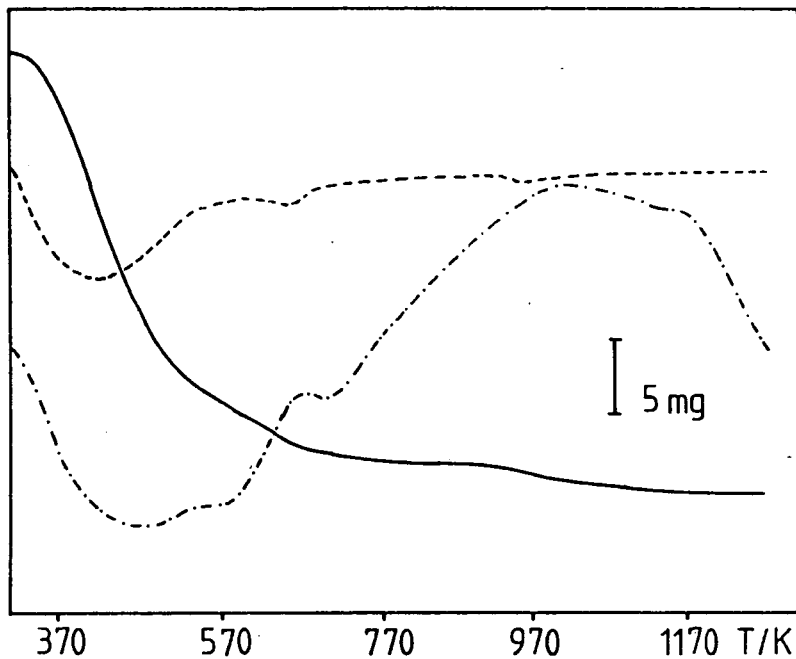
Figure 3.: Derivatographic pattern of NH_4NaY: TG ———;
DTG - - - -; and DTA -.-.-.

separated steps, at 410, 640 and 950 (as can be seen in the
DTG, too). The large and broad endotherm at 480 K (see DTA)
is due to dehydration, which is not complete prior to deam-
monization.

Under the experimental conditions used in these meas-
urements, the deammonization of NH_4NaY can be characterized
by an exotherm and an endotherm, at 580 and 660 K, respec-

tively. It was reported earlier that the deammonization of zeolites in an inert atmosphere shows no exotherm, while in the presence of oxygen there is a more or less pronounced exotherm, depending on the oxygen content of the eluent gas [20-23].

Figure 4 shows the TG curves of NaM and NH$_4$NaM. After the dehydration of NaM, no further weight loss could be ob-
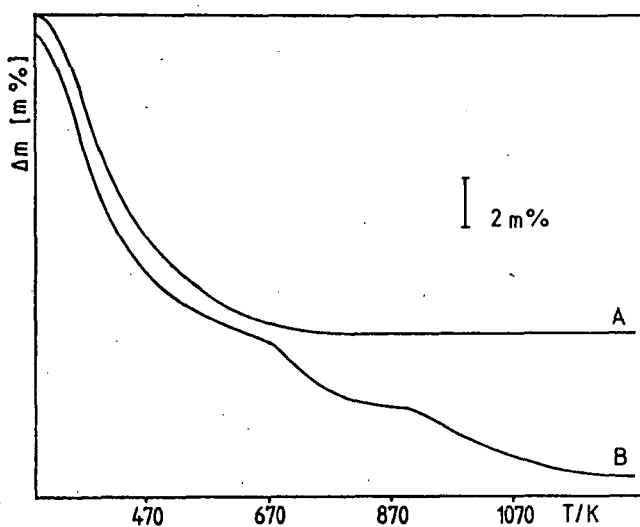

Figure 4.: TG curves of Na-mordenite (A) and NH$_4$Na-mordenite (B)

served up to 1270 K, the highest temperature obtained with our equipment. From the TG curve of NH$_4$NaM, it can be inferred that the deammonization and dehydroxylation are better

resolved then for NH_4NaY. Therefore, the ammonium ion con-
tent of this sample could be determined from the weight loss
due to deammonization (1.8 mmol/g), and was in good agree-
ment with the value derived from chemical analysis (2.1
mmol/g).

The thermal behaviour of the ZSM-5 samples is shown in
Figure 5. The TG curve of ZSM-5 "as synthesized" shows two
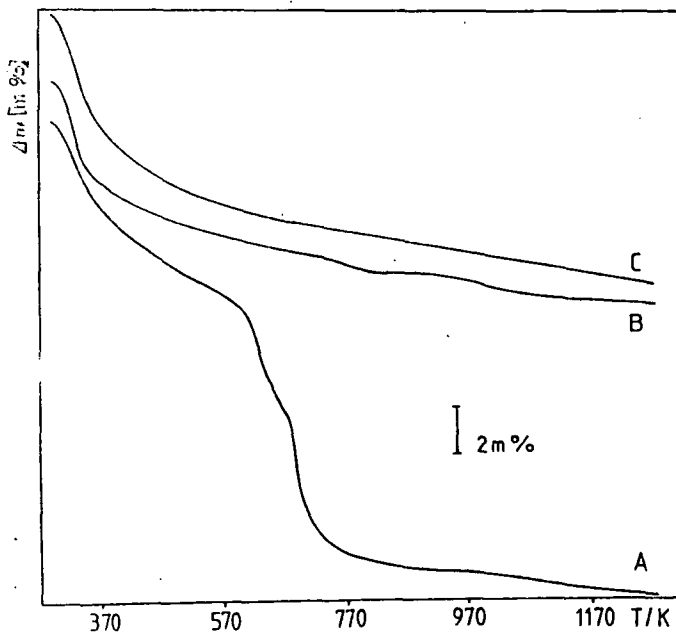overlapping steps, reflecting the weight loss upon removal

Figure 5.: TG curves of ZSM-5 "as synthesized" (A),
$NH_4NaZSM-5$ (B) and NaZSM-5 (C)

of the organic template. At higher temperatures, a slight, but continuous decrease in weight was detected. The TG curve of $NH_4NaZSM-5$ also contains two steps due to deammonization and dehydroxylation, at 770 and 1030 K, respectively, while in curve B only a slight weight loss can be observed.

Thermoanalytical investigations on NH_4NaY showed an exothermic peak at 1170 K, due to collapse of the crystal lattice. Since this temperature is much higher than that used for activation of the zeolites applied for the acidity measurements (870 K was the highest), no appreciable loss of crystallinity should be expected, although slight changes cannot be excluded. Some loss of crystallinity of NH_4NaM, which is regarded as much more stable than the Y type, was found by Weeks et al. [20]. Their explanation was that deposition of amorphous alumina takes place upon heat treatment, and simultaneously a unit cell contraction occurs. Details on the compositions of aluminium compounds formed upon different heat treatments were given by Barrer [64].

Upon the pretreatment of NH_4 forms of zeolites in high vacuum, similar transformations occur in the framework as under deep- or shallow-bed conditions, but there can be large deviations as concerns the extents of these reactions. Removal of aluminium from the framework of ZSM-5 can also take place during treatment at high temperatures. However, in our case, where each unit cell of ZSM-5 contains approximately only one aluminium ion, the formation of multinuclear aluminium complexes may be excluded for topological reasons.

Acidity measurements

In general, two main types of hydroxy groups can be distinguished in zeolites. The first type absorbs in the range 3730-3750 cm^{-1} and is assigned to nonacidic OH groups, the origin of which is still ambiguous [24, 25]. The second type concerns the acidic OH groups, as these can easily react with base molecules such as pyridine [26-29], piperidine [30], alkylamines [31, 32], etc. Depending on the type of zeolite, the cations introduced by ion-exchange and the pretreatment conditions, one or more acidic OH groups are formed in the zeolite, as proved by the respective number of ir bands in the OH stretch region [33-39].

There are two possible ways to characterize Brönsted acidity. The first is to measure the intensities of the OH bands themselves. Although this method seems to be rather approximate, and can provide only some ideas on the trend of the change in acidity for the same zeolitic type and cation form, some very careful investigations are to be found in the literature, the aim of which was to make this method more accurate [40, 41].

The second way to analyse the surface acidities of both Brönsted and Lewis sites is based on the selective adsorption of bases on both types of sites, giving rise to distinct ir absorptions. Various bases have been used as probes for the characterization or quantitative determination of the concentrations of acidic centres in zeolites [25, 42-48]. Selection of the most suitable probe molecule seems to be very difficult, since each procedure has certain disadvantages. As pyridine has been used for decades for this purpose, and as there is a great body of literature
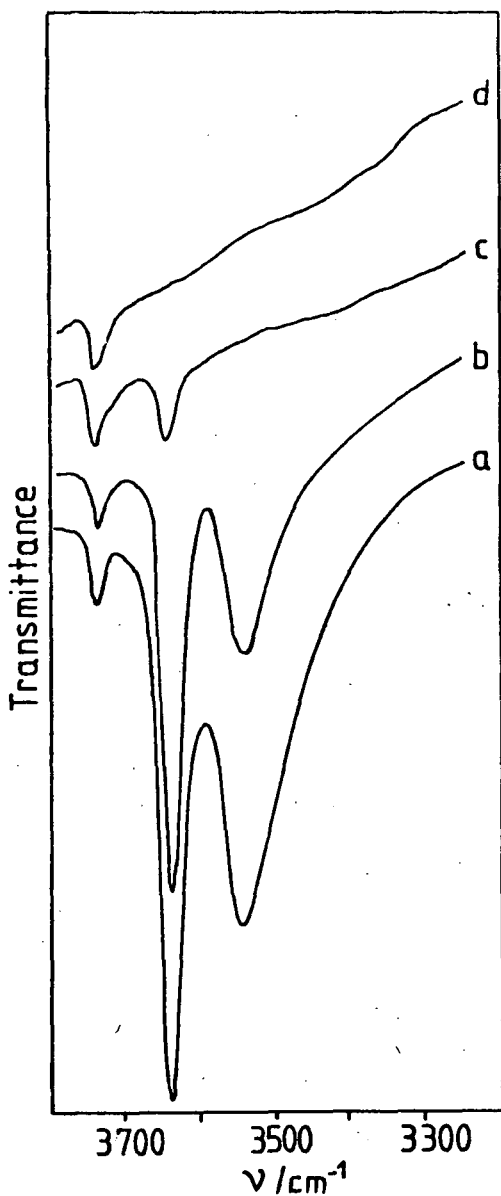
supplying a very
good and useful
background of know-
ledge, this "tradi-
tional" molecule
was chosen for our
investigations. It
should be mentioned
that the literature
contains no uniform
procedure which
could be regarded
as a standard method
with pyridine.

Self-supporting
wafers 5-7 mg/cm^2 in
thickness were pre-
pared, inserted into
a gold holder, and
placed in the ir cell
connected to the
vacuum/dosing system.

Figure 6.: Ir spectra
in the range of OH
stretching vibrations
of the H3Y sample
treated in vacuo at
450 (a), 670 (b),
770 (c) and 870 K (d)

The specimens were degassed for 12 h at different tempera-
tures in high vacuum. The final pressure was lower than
5×10^{-7} Torr. The spectra were recorded at beam temperature
with a PERKIN-ELMER 225 spectrometer

Figure 6 shows the spectra of H3Y activated at 450, 670,
770 and 870 K. For the sample evacuated at 450 K, OH bands
were detected at 3740, 3650 and 3550 cm^{-1}. Upon elevation of
the activation temperature, the bands at 3650 and 3550 cm^{-1}
decreased as a result of dehydroxylation, the Brönsted sites
being converted into Lewis sites. After evacuation at 770 K,
only the high-frequency band at 3650 cm^{-1} and the nonacidic
OH band at 3740 cm^{-1} were observed. Treatment in high vacuum
at 870 K resulted in an almost complete disappearance of
acidic OH groups. From this it should be concluded that this
sample did not contain any Brönsted acidity, although, as
will be demonstrated later, this assumption proves to be only
a very approximate one.

Adsorption of pyridine was carried out at beam tempera-
ture. In order to accelerate this process, the wafers were
treated with pyridine at temperatures high enough for com-
plete pyridine chemisorption. For zeolites Y and ZSM-4 450 K
was chosen, and for mordenite 570 K.

With the exception of mordenite, whose acidity had been
investigated very carefully by Karge, the temperature of
pyridine desorption was studied, too [49, 50]. As the con-
centration of acid sites is calculated from the absorbance
of Brönsted- (BPy) and Lewis-bound pyridine (LPy), which
depends strongly on the desorption temperature used, deter-
mination of the optimum conditions for pyridine desorption
seemed to be of high importance.

Figure 7 shows the integral absorption of BPy and LPy
as functions of the desorption temperature. It can be seen

that pyridine is desorbed more easily from Brönsted sites
than from Lewis sites with increasing temperatures. Similar
results were obtained for ZSM-5 samples pretreated at 670
and 770 K. On the basis of these investigations, 530 K was
chosen as the temperature for the desorption of pyridine.

Beamont et al. published an excellent paper on the
acidities of Y-type zeolites with different aluminium con-
tents [51]. The ready desorption of BPy was observed above
570 K. In high vacuum, after the pyridine had been pumped
off for 1 h at 450 K, some physically adsorbed pyridine re-
mained on the sample, which was not the case at 530 K. There-
fore, for Y-type zeolites 530 K was used as the temperature
for desorption.

For the determination of mordenite acidity, the Karge
procedure could be applied [49, 50], with desorption at
470 K.

Upon the adsorption of pyridine on the activated sam-
ples at beam temperature; numerous ir absorption were de-
tected, from which the bands at 1540 and 1450 cm^{-1} are as-
signed to the BPy and LPy, in accordance with the literature
[52-56]. In addition, a third band, at 1490 cm^{-1}, due to an
overlapping band of pyridine interacting with Brönsted and
Lewis acid sites, is also frequently used for analysis [57].
Figure 8 shows ir absorptions upon the adsorption of 1.33
kPa pyridine for 1 h at beam temperature on Y-type zeolites
degassed at different temperatures.

As a result of the adsorption of pyridine on NaY at
beam temperature, sharp bands were obtained at 1445, 1490,
1577 and 1623 cm^{-1}. They disappeared almost completely upon
evacuation at 530 K, where only very weak bands remained,
proving that this sample contained only few Lewis acid sites
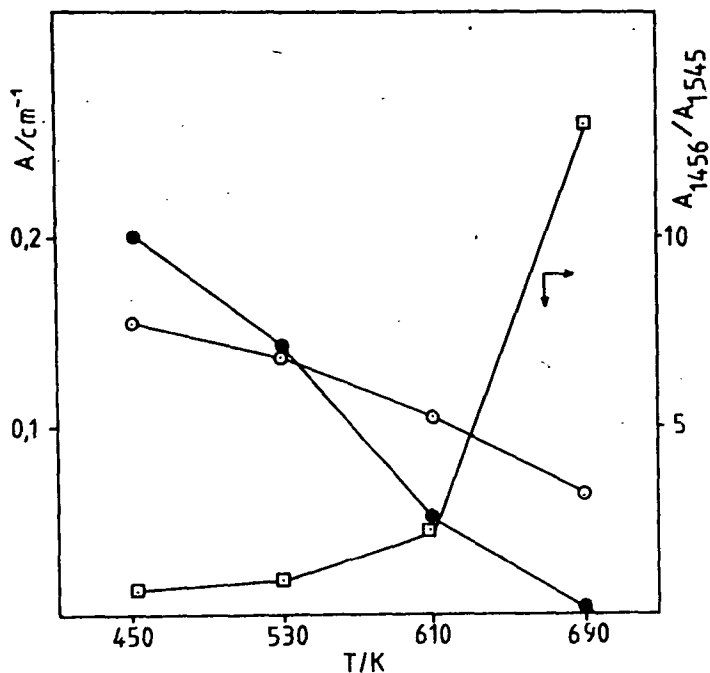(see Figure 8, spectrum a). Pyridine bound to Na^+ ions, giv-

Figure 7.: Integral absorbance of the bands of Lewis- and
Brönsted-bound pyridine and their ratio as func-
tions of the desorption temperature.

○ BPy

● LPy

□ Ratio of LPy to BPy

ing rise to a band at 1445 cm^{-1}, could be removed by evacua-
tion at 530 K for every sample tested, as seen in Figure 8.
After desorption of pyridine from HY zeolites pretreated at
different temperatures, bands characteristic of Brönsted
(1540 cm^{-1}) and Lewis (1455 cm^{-1}) acid sites were observed,
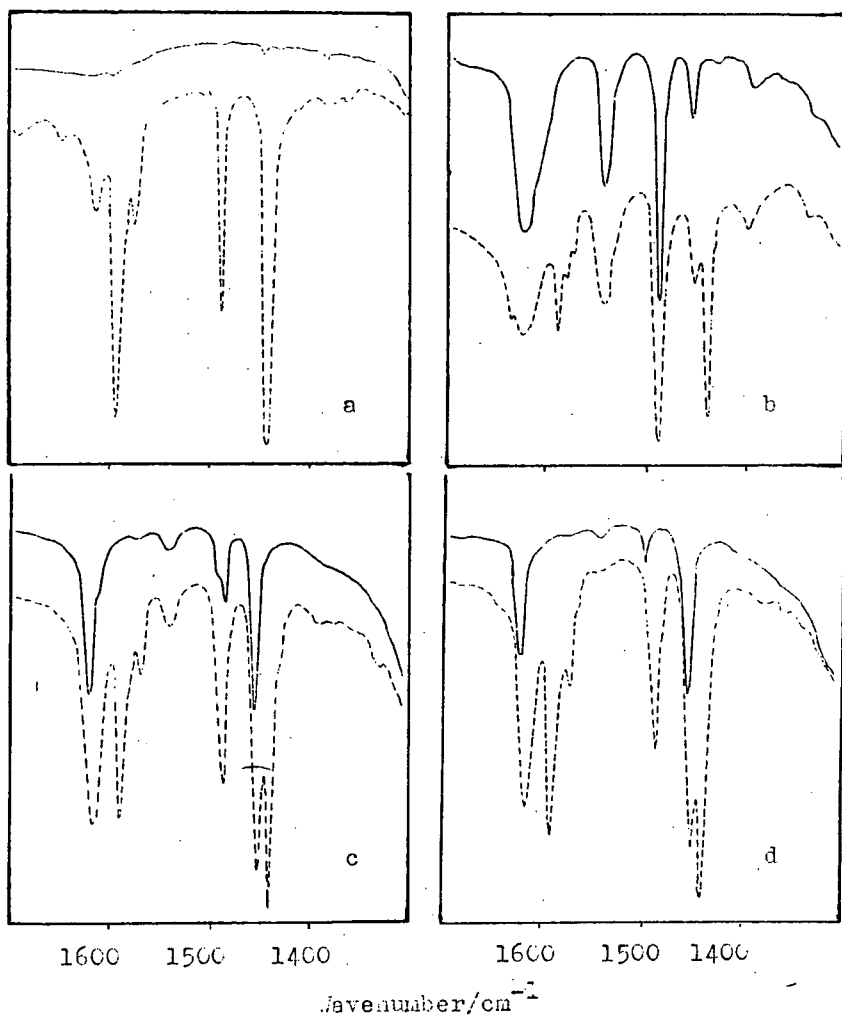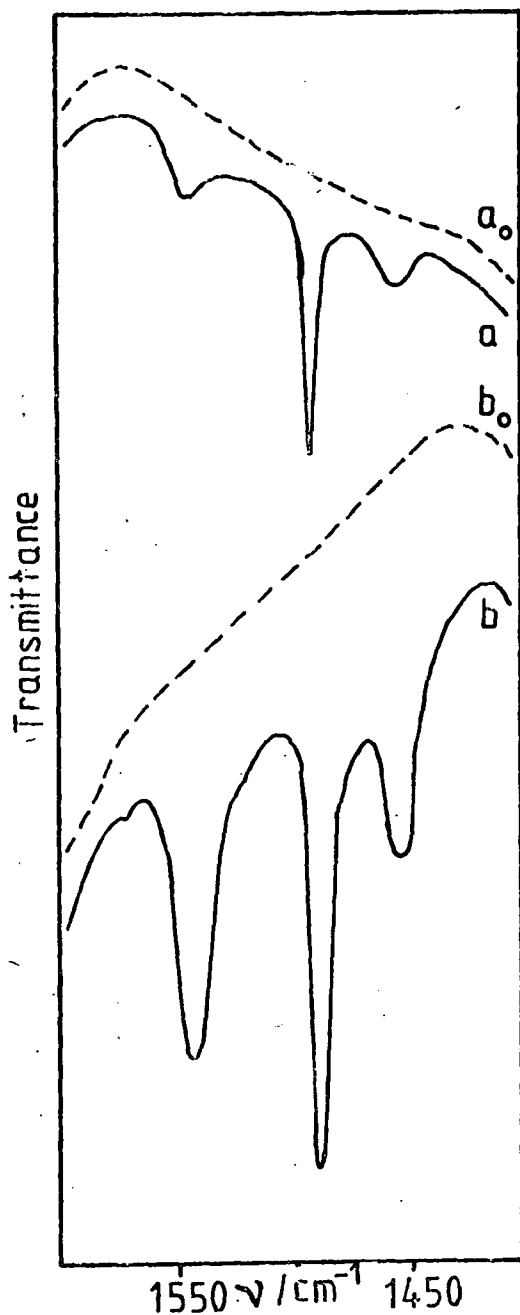the intensities of which varied with the activation tem-

Figure 8.: Ir absorption due to adsorbed pyridine on Y-type
zeolites (a) NaY, (b-d) H3Y activated at 670, 770
and 870 K. Dashed-line spectra and full-line
spectra refer to adsorbed pyridine before and
after evacuation at 410 K.

Transmittance

1550 ν /cm⁻¹ 1450

perature. In case
of the sample pre-
treated at 870 K
in high vacuum,
the BPy band could
be observed too,
although no acidic
OH bands could
be detected in the
ir spectrum. This
proves that the
application of
probe molecules
improved the sensi-
tivity of detection
of surface acidity.

Figure 9.: Infrared
spectra of ad-
sorbed pyridine
on zeolites
HZSM-5 and H-
-mordenite. a_o
and a: spectra
of HZSM-5 be-
fore and after
pyridine adsorp-
tion; b_o and
b: spectra under
similar condi-
tions for H-
-mordenite.

In Figure 9, spectra of adsorbed pyridine on H-mordenite and HZSM-5 can be seen. In both cases, Brönsted and Lewis acid sites were detected. Comparison of the band intensities shows that the concentration of acid centres is higher for mordenite than for ZSM-5.

The band frequencies of adsorbed pyridine for the investigated zeolites are listed in Table III.

Table III

Band frequencies of adsorbed pyridine for the studied samples (cm^{-1})

	Zeolite		
	HZSM-5	HNaM	HNaY
BPy	1545	1542	1545
LPy	1456	1454	1454

Estimation of the concentrations of acid sites from the spectra of adsorbed pyridine

The integral absorbance of a band between ν_1 and ν_2 is given by

$$E_{int} = \int_{\nu_1}^{\nu_2} \log (T_0/T) \, d\nu \qquad (1)$$

This represents a more unobjectionable measure for absorption and is correlated with the absorbance E_ν:

$$E_\nu = \log (T_0/T) \qquad (2)$$

where T_0/T is the ratio of the intensities of the incident

and transmitted radiation. The concentration c of the ab-
sorbed species can be determined via the Beer-Lambert law:

$$c = E/\epsilon \cdot l \tag{3}$$

where l is the path length and ϵ the extinction coefficient.
In the case of self-supporting wafers, the molar amount per
square area d (or, if more convenient, the mass per square
area) can be used in place of $c \cdot l$, by means of which the
extinction coefficient

$$\epsilon_\nu = E_\nu/d \qquad [m^2 \cdot mol^{-1}] \tag{4}$$

or the integral extinction coefficient

$$\epsilon_{int} = E_{int} = d \qquad [m \cdot mol^{-1}] \tag{5}$$

can be determined.

The following factors influence the accuracy of
determination of the number of acidic centres. The determi-
nation of band intensities is usually straightforward, but
for zeolites where the spectrum is obscured by additional
bands of framework vibrations in the range 1400-1600 cm^{-1},
more attention should be paid to the establishment of the
baseline. Furthermore, determination of the extinction coef-
ficient of a surface species is in general difficult, as the
simultaneous measurement of ir intensity and adsorbed amount
is necessary, provided that only one surface compound is
formed. If the extinction coefficients were identical for
both species of adsorbed pyridine the ratio of the band ab-
sorbances would yield the ratio of the concentrations of
Brönsted and Lewis acid sites. However, this is generally not

the case, and different approaches have been used to over-
come this problem. A number of papers deal with this funda-
mental question; of these only the most important will be
mentioned, in order to show the great efforts which had to
be made in this field.

Ward suggested utilization of the fact that, upon heat
treatment, two Brönsted acid sites are converted into one
Lewis acid site, keeping the sum of 2 Lewis sites + 1 Bröns-
ted site constant, while their ratio will change with the
temperature of pretreatment [58]. Thus, from measurements
of pyridine adsorption on two samples activated at different
temperatures, $\varepsilon_L/\varepsilon_B$ and the ratio of acid sites can be de-
termined. This method was succesfully applied to Y-type
zeolites, but it cannot be applied to mordenites, where this
conversion does not follow the stoichiometry mentioned above.

Basila and co-workers studied the contributions of LPy
and BPy to the intensity of the common band at 1490 cm^{-1}
[59]. For investigations on potassium-poisoned silica-
-alumina, the ratio of the extinction coefficients
$\varepsilon_{1490}/\varepsilon_{1450}$ was found to be 0.25 and the ratio of Lewis to
Brönsted acid centres was estimated via

$$\frac{LPy}{BPy} = \frac{1.5 \ E_{1450}}{E_{1490} - 1.5 \ E_{1450}}$$

Recently, Riseman et al. reinvestigated this problem
[60], and the relationship

$$\frac{LPy}{BPy} = \frac{6.035 \ E_{1450}}{E_{1490}^T - 0.35 \ E_{1450}}$$

was found to be valid, where E^T_{1490} means the total ab-
sorbance of the 1490 cm^{-1} band. From a comparison of these
two equations, their analogy becomes obvious. Although the
applicability of this method (based on the assumption that
the ratio of the extinction coefficients $\varepsilon_{1490}/\varepsilon_{1450}$ is
the same for alumina, silica-alumina and zeolites) seems to
be proved, the fundamental question of whether the extinc-
tion coefficients of BPy and LPy are independent of the
strengths of the acid sites present in different solids has
not been completely clarified.

Direct determination of the extinction coefficients of
LPy and BPy requires two extremely different samples, one
containing only Brönsted, and the other only Lewis acidity.
Preparation of these samples is difficult, though not impos-
sible [50]. With these samples available, the extinction
coefficients can be determined. This was done by Datka, who
obtained 0.084 and 0.059 cm^2/μmol for BPy and LPy, respec-
tively, on HNaY [61], and 0.058 cm^2/μmol for LPy on HNaZSM-5
[62]. These nearly identical values of LPy support the above
assumption that it is almost independent of the zeolite
(and/or silica-alumina). In constrast to Datka's results,
Stock et al. obtained significant differences as concerns
the extinction coefficients of BPy even for zeolites HNaY
and HNaX [40].

Take determined the extinction coefficients of BPy and
LPy for HZSM-5. The value for BPy was similar to those of
Stock et al. and Hughes and White [30], but that for BPy was
somewhat smaller than that for LPy [63].

Table IV. lists the extinction coefficients found in
the literature.

Table IV

Extinction coefficients of pyridine adsorbed on Brönsted and Lewis acid sites, taken from the literature

B	L	References
0.084 cm^2/μmol	0.059 cm^2/μmol	61
–	0.058 cm^2/μmol	62
1.31 cm/μmol	1.42 cm/μmol	30
1.11-1.49 cm/μmol	–	40
1.3 cm/μmol	1.5 cm/μmol	63

It was difficult to select the extinction coefficients for both kinds of surface acidity and the procedure for their determination from the literature. Finally, we chose the integral extinction coefficients published by Take [63], simply because these were the most recent data in the literature. The concentrations of acid sites calculated as described in this paper can be found in Table V. for the zeolites applied.

Our acidity measurements permit the conclusion that the higher the ammonium ion content of the sample, the larger the number of acid sites formed in the zeolite during deammoniation.

For mordenite and zeolites Y, it was found that the concentration of Lewis acid sites passes through a maximum at 770 K with increasing pretreatment temperature. The same was found by Karge for zeolite NH_4M [50]. According to his explanation, the reason for the decrease in Lewis acidity above 770 K is that the increasing amount of $[AlO^+]$ species formed during dehydroxylation hinders the diffusion of pyr-

Table V

Concentrations of acidic sites for the zeolites tested
in this study

Sample	Temperature of vacuum treatment	Concentration of acid sites in mol/kg	
		Brönsted	Lewis
NaY	770	–	detectable
H1Y	670	0.078	0.013
H2Y	670	0.275	0.093
H2Y	770	0.014	0.151
H3Y	670	0.441	0.082
H3Y	770	0.058	0.305
H3Y	870	0.007	0.156
HM	670	0.695	0.193
HM	770	0.212	0.460
HM	870	0.023	0.182
HZSM-5	670	0.033	0.008
HZSM-5	770	0.028	0.013
HZSM-5	870	0.018	0.015

_idine in the pore system of mordenite. Recently, Shannon et al. investigated the nature of the nonframework aluminium species in HY zeolite [65], and concluded that similar residual nonframework aluminium species are present in both HY dehydroxylated at 920 K in vacuo and HY steamed at 1160 K. However, in the latter in increased degree of con-densation and an increased number of nonframework aluminium species were found. A boehmite-like phase could be identified, which is present in the supercages and has dimensions fitting the supercage of Y-type zeolites.

This boehmite-like phase can be formed through the cluster-
ing of smaller Al-containing species during dehydroxylation.
These results indicate that dehydroxylation is accompanied
by condensation of aluminium-containing species (at least
of boehmite structure). Therefore, the higher the tempera-
ture, the greater the degree of condensation and consequent-
ly, the more increased the hindrance for pyridine diffusion,
even in the case of HY zeolite. On the other hand, if the
species formed during dehydroxylation are not large enough,
they could act as multiple adsorption sites for two or
three pyridine molecules. However, as these types of inter-
actions are improbable because of steric hidrance, the
decreasing number of Lewis acid sites above 770 K seems to
be explainable in terms of the formation of aluminium-con-
taining clusters.

Summary

Zeolite catalysts have been characterized by X-ray dif-
fraction, derivatography and ir spectroscopy. The X-ray
measurements showed that the crystallinity of the tested
zeolites was well-preserved. Ir spectroscopic investigations
in the range of framework vibrations supplemented this find-
ing. The absorptions observed for these samples are in good
agreement with literature data.
    The acidities of the zeolites were determined by means
of pyridine adsorption. For mordenite and zeolite Y, the
number of Lewis acid sites passed through a maximum at 770 K,

while a monotonous decrease in the number of Brönsted acid
sites was found with increasing pretreatment temperature.
The decrease in the number of Lewis acid centres above
770 K was explained by the enhanced formation of nonframe-
work aluminium-containing clusters generated during
dehydroxylation.

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ИЗУЧЕНИЕ КИСЛОТНОСТИ ЦЕОЛИТОВ РАЗНОГО ТИПА

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Определены характеристики различных цеолитов с помощью рентгеновской дифракции, дериватографии и инфракрасной спектроскопии. Кислотность цеолитов определялась адсорбцией пиридина. Критически рассмотрены литературные данные, относящиеся к адсорбционным коэффициентам пиридина на кислых местах цеолитов.