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Infrared Internal Reflection and Transmission Spectra of Synthetic X and Y Zeolites Containing Na^+, NH_4^+ and Ca^{2+} Cations

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The influence of the pelletizing pressure on the frequency of the O–H stretching vibration at 3640 cm^{-1} has been studied up to 7000 kp/cm^2 for CaY and NH_4-Y zeolites by means of internal reflection and transmission techniques. No influence of the pressure was observed concerning the frequency of the O–H stretching vibration. The comparison of internal reflection with transmission spectra of X and Y zeolite powders containing Na^+, NH_4^+ or Ca^{2+} cations revealed no difference in the frequency of the O–H stretching vibrations. The different intensities of the normalized band at 3740 cm^{-1} in internal reflection and transmission spectra of a NH_4-X zeolite with 0.4 and 1.9 μm particle size, respectively, support the assignment of this band to terminal OH groups.

INTRODUCTION

The ir spectroscopy is a common method for the investigation and characterization of hydroxyl groups on zeolites. These hydroxyl groups are considered as one type of active sites (*1,2*). Basically two types of O–H vibration bands have been detected in the infrared spectra of zeolites: the O–H stretching and deformation bands of physically adsorbed molecular water and the O–H stretching vibrations of structural hydroxyl groups (*3,4*).

Water can be adsorbed on the zeolites as associated hydrogen-bonded water with a very broad band around 3400 cm^{-1} or as isolated molecular water interacting with cations, which shows an absorption band at 3690 cm^{-1} (*5–7*). In addition to these bands due to adsorbed water the Na-X and Na-Y zeolites show O–H bands with much lower intensity. Christner *et al.* (*4*) found a weak band at 3750 cm^{-1}, Angell and Schaffer (*8*), Carter *et al.* (*3*) two bands at 3750 and 3655 cm^{-1}.

For catalytic purposes the Na forms of X and Y zeolites are not so important because they have a low concentration of hydroxyl groups, which act as active sites. By replacing the Na^+ with NH_4^+ ions and thermally decomposing the NH_4^+ ions it is possible to increase the hydroxyl concentration by the factor of 50 (*9*). Many investigations about thermally decomposed NH_4^+ zeolites (decationized) have been reported in literature (*10–18*). After a heat treatment at 400°C 3 bands were observed in the ir spectrum: at 3740 and 3640 cm^{-1} analogous to Na-X and Na-Y zeolites however with much higher intensity, and at 3540 cm^{-1}. The bands at 3640 and 3540 cm^{-1} have been correlated to OH groups in the supercage and cubooctahedron (*1*). However, the assignment of the 3740 cm^{-1} band is not yet clear. Some authors assign it to terminal hydroxyl groups on the external surface (*19*). Others believe that occluded impurities of silica are responsible for this band (*8*).

Another possibility to modify the catalytic behavior is to exchange the Na^+ with Ca^{2+} ions. Many investigations have been reported about Ca-exchanged zeolites (*3,4,8,19–22*). The two additional O–H bands at 3690 and 3585 cm^{-1} of the Ca-exchanged zeolites correspond to water and hydroxyl groups both attached to Ca^{2+} cations.

All these investigations were carried out by means of the transmission technique. The samples were pressed under high pressures (700–7000 kp/cm^2) to form infrared transparent pellets of 5–30 mg/cm^2. Using this technique the samples are not examined in their natural state as powders. The compression can change the adsorption behavior by creating an additional secondary pore structure between the primary particles. All these investigations on zeolites assume that the compression does not have any influence on the catalytic activity and adsorption behavior. However, on amorphous silica (*23*) it was shown, that the pelletization causes changes in the infrared spectrum. The superficial functional groups of the particles interact with each other because of the small distances.

The internal reflection spectroscopic method allows one to investigate the samples in the natural state without any losses of light by scattering (*24–26*). Contrary to the transmission method the internal reflection technique scans regions only on or near the surface. Using both methods it might be possible to draw conclusions concerning the differences of hydroxyl groups on the interior and external surface.

The aim of the present investigation was to study the influence of compression on the frequency of OH groups on zeolite particles and to obtain more evidence for a proper correlation of the 3740 cm^{-1} band. For this purpose infrared spectroscopic studies were carried out using the internal reflection and the transmission techniques. In both methods the zeolite samples were employed as powders. The obtained data were compared with spectra of compressed pellets known from literature and with spectra of self-prepared pellets. To obtain more detailed information about the O–H stretching band at 3740 cm^{-1} transmission and internal reflection spectra of samples with different particle sizes were recorded.

EXPERIMENTAL METHODS

Materials. The 3 samples of the sodium X and sodium Y zeolites were Na-X and Na-Y (SK 40) from Union Carbide Corp. and Na-X from Bayer Germany. Analysis of the parent zeolites on anhydrous basis are given in Table 1.

The NH_4^+ zeolites and Ca^{2+} zeolites were prepared from parent sodium forms by ion exchange with 0.1 *N* solutions of analytical grade NH_4NO_3 and $Ca(NO_3)_2$ obtained from Merck, Germany. The exchanged material was washed with distilled water to free it from residual salt. The degree of ion exchange was determined by analysis for sodium by flame spectrometry. The prepared NH_4^+ zeolites and Ca^{2+} zeolites had following degrees of exchange (%): NH_4X, 75; NH_4Y, 71: CaX, 79; CaY, 70.

Procedure. All spectra were recorded on a Perkin-Elmer grating spectrophotometer Model 421 using a spectral slit width of 6 cm^{-1} and a scan speed of 60 cm^{-1}/min or 25 cm^{-1}/min for expanded spectra. The spectrophotometer including sample com-

TABLE 1
ANALYSIS OF ZEOLITES

Sample	SiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	Av particle size (μm)
Na-X (Bayer)	47.5	32.9	19.6	0.4
Na-X (Union Carb.)	48.0	32.4	19.6	1.9
Na-Y (Union Carb.)	63.5	23.5	13.0	1.2

partment was purged with dry and CO_2-free air during measurements. The radiation emitted from heated reflection plate and the sample was checked and found to have no influence on the spectra at the appropriate temperatures.

The internal reflection spectra were obtained with an optically balanced double beam system consisting of two modified high vacuum heatable reflectance chambers Model 38 B from Wilks Scientific Corp., USA with CaF_2 windows. The single pass multiple reflection plates of silicon with 50 reflections at an angle of incidence of 45° in each plate were also from Wilks.

For the transmission studies 2 home-built infrared cells described elsewhere (*27*) with CaF_2 windows were used. The zeolite samples were also examined as powders by sprinkling them between two Irtran-2 plates, as developed by Ahmed and Gallei (*28*). The pellets were prepared by pressing roughly 15 mg of zeolite powder under various pressures in a steel die.

TABLE 2

O–H STRETCHING FREQUENCIES OF NH_4-EXCHANGED ZEOLITES IN TRANSMISSION SPECTRA (PELLETS) FROM LITERATURE

Refs.	Activation temp (°C)	Pelletizing pressure (kp/cm^2)	Wavenumber (cm^{-1})		
		NH_4-X			
(*29*)	400	7000	3690	3658	
(*14*)	500	200		3650	3550
(*2*)	480	1000	lattice partially destroyed		
(*22*)	490	—		3650	
(*17*)	300	1000		3665	3550
		NH_4-Y			
(*16*)	480	—	3750	3640	3540
(*19*)	400	1400	3742	3643	3540
(*11*)	380	1400	3742	3643	3540
(*10*)	700	1400	3742	3643	3540
(*15*)	480	1400	3742	3640	3540
(*13*)		700		3649	3550
(*30*)	350	700		3648	3550
(*8*)	500	700	3744	3636	3544
(*31*)	250	400		3677	3567
(*30*)	400	1000		3650	3550
(*32*)	300	360	3745	3650	3545
(*14*)	500	200		3650	3550

The samples both in the internal reflection and in the transmission cell were heated gradually (1°C/min) and maintained at the appropriate temperature (±1°C) by a home-built heat-controller. Both cells were connected to a high vacuum system. Up to 250°C the spectra were recorded at the pretreatment temperature. At higher activation temperatures it was necessary to cool the samples down to 250°C because the internal reflection plates became opaque above this temperature. Transmission spectra could be recorded easily at temperatures higher than 250°C. The spectra were recorded at the following activation temperatures: 40, 100, 150, 200, 250, 300, 350 and 400°C. The activation time was 1 hr for all temperatures.

RESULTS AND DISCUSSION

Influence of the Pelletizing Pressure

Many investigations on X and Y zeolites containing Na^+, NH_4^+ or Ca^{2+} ions by means of the pellet technique have been reported in literature. The results are listed in Tables 2–4.

The obtained internal reflection spectra of powdered Na-X and Na-Y zeolites (Table 5) show that these spectra cannot be compared with those of the appropriate pelletized samples. The concentration of structural OH groups on the sodium zeolites is so small, that we do not observe in the internal reflection spectrum the corresponding absorption bands of the O–H stretching vibrations. Even with transmission techniques one obtained frequently only water absorption bands (Table 3).

The Ca^{2+} and NH_4^+ forms of the zeolites X seem also little useful for a comparison between internal reflection and transmission spectra regarding the frequencies of the O–H stretching vibrations.

Because of the high activation temperatures up to 500°C (Tables 2–4) used with the transmission methods the lattice framework of the X zeolites is partially destroyed as it was shown from Ward (*2*) by X-ray analysis. The differences between the internal reflection and transmission spectra originate most probably from the partial destruction of the zeolitic framework due to the high activation temperatures, but not from the different sample preparation (powder-pellet).

Basically we have 3 O–H stretching bands available for the comparison between powder and pellet spectra: the band at 3740 cm^{-1} corresponding probably to terminal OH groups on the outer surface of the zeolite particles, the band at 3640 cm^{-1} which is due to O–H groups in the supercages and the band at 3540 cm^{-1} assigned to O–H groups located in the smaller cavities. However, the band at 3740 cm^{-1} has very low intensity and the band at 3540 cm^{-1} is fairly broad, so it is difficult to determine the exact band positions. Only the strong sharp band at 3640 cm^{-1} is left for careful evaluation. Therefore we used the Ca^{2+} and NH_4^+ forms of the zeolite Y for the comparison of internal reflection and transmission spectra observing the band position of the strong sharp band around 3640 cm^{-1}.

Figures 1 and 2 show the band position (cm^{-1}) of the O–H band around 3640 cm^{-1}

TABLE 3

O–H STRETCHING FREQUENCIES OF Na-EXCHANGED ZEOLITES IN TRANSMISSION SPECTRA (PELLETS) FROM LITERATURE

Refs.	Activation temp (°C)	Pelletizing pressure (kp/cm²)	Wavenumber (cm^{-1})					
			Na-X					
(*21*)	225	—		3685		3543		
(*2*)	480	1000	No OH bands					
(*33*)	450	—	No OH bands					
(*29*)	-400	7000		3695				
(*8*)	500	700	3744					
(*34*)	500	2800		3695	3650			
(*7*)	500	3650	3687	-3695			3400	3250
(*6*)	-400	—		3690			3390	3225
(*3*)	150	700	3750	3695	3655	3400	1650	
	300	700	3750	3695	3655	—	—	
	450	700	3750	3695	3655	—	—	
	600	700	3750	3695	3655	—	—	
			Na-Y					
(*36*)	400	1400	No OH bands					
(*19*)	400	1400	No OH bands					
(*21*)	100	—	3735	3690	3600	3380	3280	
	360	—	3738	3695	3588			
(*20*)	480	1400	3600	-3300				
(*6*)	-400	—	3690	3450				
(*8*)	500	700	3748	3652				

TABLE 4

O–H STRETCHING FREQUENCIES OF Ca-EXCHANGED ZEOLITES IN TRANSMISSION SPECTRA (PELLETS) FROM LITERATURE

Refs.	Activation temp (°C)	Pelletizing pressure (kp/cm^2)	Wavenumber (cm^{-1})					
			Ca-X					
(3)	200	700	3750	3695		3590		
(8)	500	700	3744					
(22)	490	—	3740	3690	3650	3550	3605	
	490	—	3740	3695	3650		3610	
(21)	500	—		3690			3610	
			Ca-Y					
(20)	500	1400	3739	3688	3642	3520	3582	
(19)	400	1400	3739	3688	3642	3540	3585	
(36)	450	—		3688	3642	3530	3585	
(21)	230	—	3740	3690	3640	3560	3590	3520
	350	—	3740	3690	3640		3590	3520
	480	—	3738	3690	3640		3585	3540
(4)	250	360	3745		3645			
(22)	490	—	3740	3695	3650		3550	
(3)	200	700	3750	3690	3650			
(8)	500	700	3746		3645			
			3748		3648		3540	

TABLE 5

COMPARISON OF TRANSMISSION WITH INTERNAL REFLECTION SPECTRA OF Na-EXCHANGED POWDERED ZEOLITES

Activation and recording temp	Wavenumber (cm^{-1})											
	Internal reflection spectra						Transmission spectra					
	Na-X											
40	—	3692	—	—	3400	1645	—	3691	—	—	3400	1640
100	—	3685	—	—	3400	1650	—	3688	—	—	3400	1645
150	—	—	—	—	3400	1655	—	3685	—	—	(3400)	1645
200	—	—	—	—	3400	(1650)	—	3683	3640	—	—	1648
250	—	—	—	—	—	—	(3740)	3680	3640	—	—	(1640)
300	—	—	—	—	—	—	(3740)	3680	3640	—	—	—
350	—	—	—	—	—	—	(3700)	3680	3640	—	—	—
400	—	—	—	—	—	—	(3700)	3680	3640	—	—	—
	Na-Y											
40	—	(3690)	—	—	3400	1640	—	3690	—	—	3400	1640
100	—	—	—	—	3400	1640	—	—	—	—	—	1650
150	—	—	—	—	—	1640	—	—	—	—	—	1650
200	—	—	—	—	—	(1640)	—	—	—	—	—	(1650)
250	—	—	—	—	—	—	—	—	—	—	—	—
300	—	—	—	—	—	—	—	—	—	—	—	—
350	—	—	—	—	—	—	—	—	—	—	—	—
400	—	—	—	—	—	—	—	—	—	—	—	—

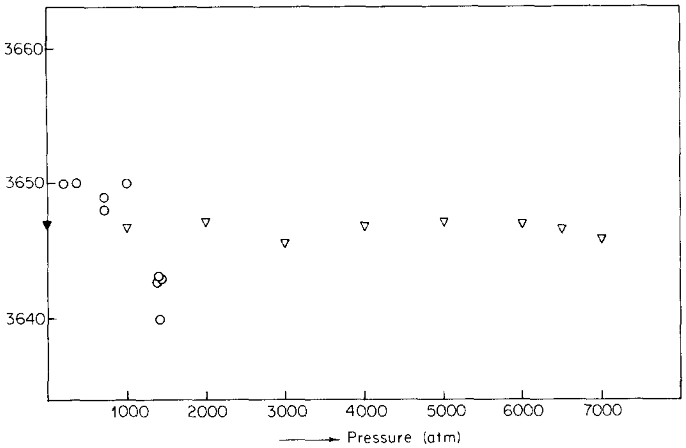

FIG. 1. Frequency of the O–H absorption band around 3640 cm^{-1} of NH_4-Y as a function of the pelletizing pressure. (▼) frequency from the internal reflection spectrum as internal standard; (○) values from literature; (▽) values from self-prepared pellets.

of the zeolites NH_4Y and CaY as a function of pressure used for pelletizing. Internal standard is the pressure $p = 0$ as it is employed in internal reflection experiments. There is no dependency observable of the band position on the pelletizing pressure. The frequencies of the internal reflection spectra are identical with the appropriate transmission spectra using pellets compressed under pressures up to 7000 kp/cm^2. These results are confirmed by investigations of Carter *et al.* (*3*), who carried out X-ray analysis for pellets (700 kp/cm^2) and powders of zeolite Y. They did not observe any change of the crystalline zeolitic structure.

The independency of the O–H frequency from the pelletizing pressure can be explained by the zeolitic crystal structure itself. The OH groups in zeolites are distributed on the internal and external surfaces. However, the external surface area is only approximately 1% of the total surface area. Under the assumption of a fairly equal distribution most OH groups should be located on the internal surface.

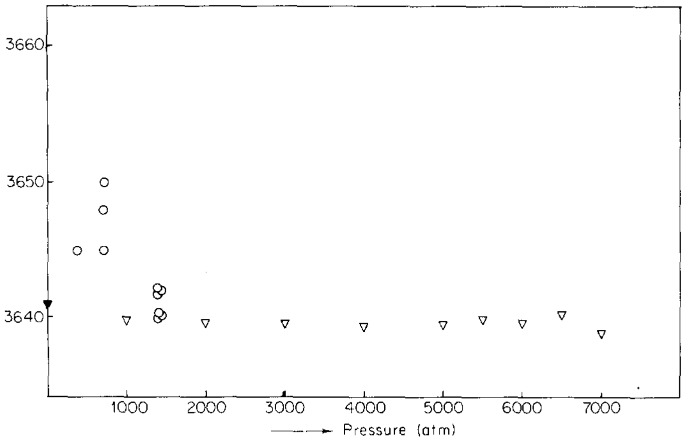

FIG. 2. Frequency of the OH absorption band around 3640 cm^{-1} of Ca-Y as a function of the pelletizing pressure. (▼) frequency from internal reflection spectrum as internal standard; (○) values from literature; (▽) values from self-prepared pellets.

TABLE 6

Comparison of Transmission with Internal Reflection Spectra of NH_4-Exchanged Powdered Zeolites

Activation and recording temp	Wavenumber (cm^{-1})													
	Internal reflection spectra							Transmission spectra						
							NH_4-X							
40	3740	3666	3563	3400	3200	1678	—	3740	3663	3550	3400	3200	1640	1430
100	3740	3657	3566	3400	3200	1675	—	3740	3660	3550	3400	3200	1650	1430
150	3740	3653	3569	—	—	—	—	3740	3653	3550	3400	3200	1680	1430
200	3740	3652	3568	—	—	—	—	3740	3650	3560	3400	3200	1680	1430
250	3740	3648	3568	—	—	—	—	3740	3648	3560	—	3200	—	1430
300	3740	3648	—	—	—	—	—	3740	3648	3560	—	—	—	1430
350	3740	3649	—	—	—	—	—	3740	3648	3560	—	—	—	—
400	3740	3648	—	—	—	—	—	3740	3648	3560	—	—	—	—
							NH_4-Y							
40	—	(3655)	(3540)	3400	3200	1665	—	—	3655	—	3385	3200	1645	1450
100	—	3648	3540	3400	3200	1665	—	—	3650	3550	3393	3200	1665	1430
150	—	3643	3540	—	—	(1660)	—	—	3646	3543	3396	3200	1670	1430
200	—	3639	3540	—	—	—	—	—	3645	3542	3397	3200	1670	1430
250	—	3638	3540	—	—	—	—	—	3640	3540	3397	(3200)	1670	1430
300	—	3637	3540	—	—	—	—	—	3640	3540	—	—	—	1430
350	—	3638	3540	—	—	—	—	—	3639	3540	—	—	—	1430
400	—	3638	3540	—	—	—	—	—	3640	3540	—	—	—	(1430)

TABLE 7

Comparison of Transmission with Internal Reflection Spectra of Ca-Exchanged Powdered Zeolites

Activation and recording temp	Wavenumber (cm^{-1})											
	Internal reflection spectra							Transmission spectra				
							Ca-X					
40	—	—	(3640)	—	—	1620	—	3690	—	—	—	1648
100	—	—	3642	—	—	1620	—	3685	3645	3612	—	1620
150	—	—	3642	—	—	(1600)	(3740)	3690	3645	3611	3565	1625
200	—	—	3640	—	—	(1600)	3740	3685	3642	3605	3560	1632
250	—	—	3638	—	—	—	3740	3685	3640	3605	3560	1632
300	—	—	—	—	—	—	3740	3680	3638	3600	(3560)	1635
350	—	—	—	—	—	—	3740	3680	3638	3600	—	(1635)
400	—	—	—	—	—	—	3740	3680	3638	3600	—	—
							Ca-Y					
40	—	—	—	—	—	1640	—	3690	—	—	—	1638
100	—	—	3640	—	—	1650	—	3690	—	3610	—	1642
150	—	—	3635	—	—	(1650)	—	(3690)	—	3610	—	1650
200	—	—	3632	—	—	—	—	—	3633	—	3550	1653
250	—	—	3630	—	—	—	—	—	3632	—	(3550)	1650
300	—	—	(3630)	—	—	—	—	—	3631	—	—	(1650)
350	—	—	—	—	—	—	—	—	3630	—	—	—
400	—	—	—	—	—	—	—	—	3632	—	—	—

A disturbance or mutual interaction of the internal OH groups, which are shielded by the zeolite framework, is only possible by a change of the crystal structure. The pelletizing pressures up to 7000 kp/cm^2 do not seem high enough to cause such crystal deformations. However, the data from literature scatter over a wide range. All these spectra were recorded at sample beam temperature. But the temperature of the sample beam is very undefined and varies probably in the various investigations. The different methods of preparation and activation of the samples should also influence the frequency of the OH band around 3640 cm^{-1}.

Comparison Between Internal Reflection and Transmission Spectra of X and Y Zeolite Powders

In the previous section transmission data obtained with compressed pellets have been compared with results from the internal reflection technique. To investigate the influence of the pelletizing pressure on the band position of the O–H stretching vibrations we have to exclude any effect originating from the different spectroscopic techniques (transmission–reflection). Therefore we compared our internal reflection spectroscopic data with transmission spectra obtained on powdered samples by means of a technique described elsewhere (*28*). The results are listed in Tables 5–7 for X and Y zeolites containing Na$^+$, NH$_4{}^+$ and Ca^{2+} cations. The tables show OH stretching bands and in addition bands due to molecular adsorbed water. The latter, however, disappear at higher activation temperatures. The spectra obtained from internal reflection and transmission technique are identical concerning the band position of the OH stretching vibrations (Fig. 3). However, a fundamental difference exists between internal reflection and transmission spectra. The weak absorption bands observable in the transmission spectra are

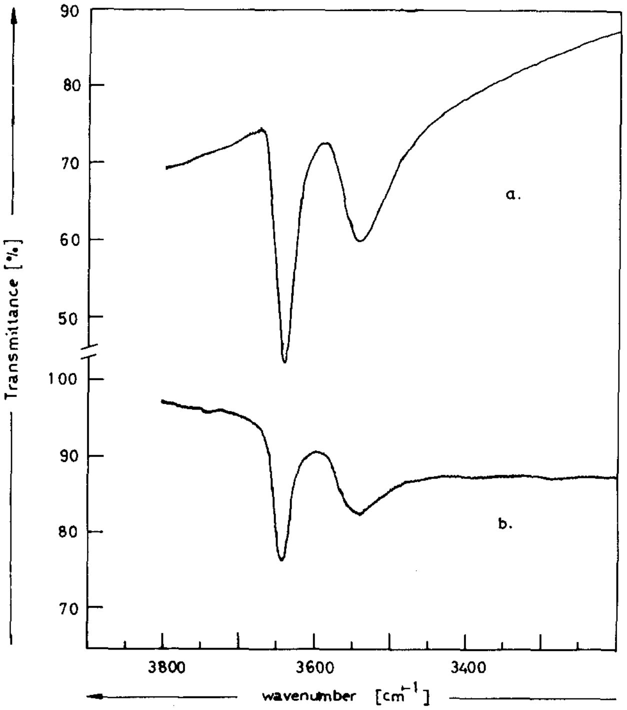

FIG. 3. Transmission (a) and internal reflection (b) spectrum of decationized Y zeolite.

missing in the appropriate internal reflection spectra. The reason of the absence of the weak bands in the internal reflection spectra as obtained by the method of internal reflection technique is the small amount of sample (~ 1 mg) interacting with the infrared beam. The depth of penetration into the sample of the evanescent wave established near the totally reflecting interface amounts approximately to 0.3 μm with our silicon internal reflection elements in the OH stretching range. The amount of sample penetrated by the infrared beam in the transmission method is much higher (~ 5 mg).

From our results one can conclude that the internal reflection technique is a valuable supplement to the common transmission methods. The internal reflection technique can be successfully employed where the transmission methods fail, e.g., for samples with high scattering losses like quartz (*26*) or strongly absorbing materials (*35*), which make up most technical catalysts. A further advantage of the internal reflection technique is that one can examine also samples with particle sizes in the same order of magnitude or even larger than the wavelength of the interfering light.

Investigation on NH_4-X Zeolites with Different Particle Sizes

In literature there is still some controversy concerning the band around 3740 cm^{-1}. Angell and Schaffer (*8*) discussed the possibility of assigning it to crystal surface groups, occluded silica impurities or defective sites. Ward (*19*) assigned this band to Si–O–H groups terminating the lattice. Using transmission and internal reflection methods for zeolites with different particle sizes it should be possible to give more evidence for a proper assignment of this band around 3740 cm^{-1}. In the case of the transmission method the sample is completely penetrated by the infrared light. With internal reflection spectroscopy, however, only regions on or near the surface are scanned (*36*). Therefore we recorded the transmission (powders) and internal reflection spectra of two NH_4-X zeolite samples with an average particle diameter of 0.4 and 1.9 μm, respectively, between 100 and 400°C.

If the 3740 cm^{-1} band is correlated to terminal O–H groups on the external surface of the crystals one should obtain the following results for zeolites with different

TABLE 8

INTENSITIES OF THE NORMALIZED BAND AROUND 3740 cm^{-1} IN TRANSMISSION AND INTERNAL REFLECTION SPECTRA OF NH_4-X ZEOLITES WITH TWO DIFFERENT PARTICLE SIZES[a]

Activation and recording temp (°C)	Transmission		Internal reflection	
Av particle diam (μm):	0.4	1.9	0.4	1.9
100	5.9×10^{-2}	0.9×10^{-2}	6.7×10^{-2}	2.4×10^{-2}
150	12.1×10^{-2}	1.0×10^{-2}	9.1×10^{-2}	3.2×10^{-2}
200	10.0×10^{-2}	1.0×10^{-2}	13.5×10^{-2}	3.8×10^{-2}
250	9.3×10^{-2}	1.0×10^{-2}	12.7×10^{-2}	5.2×10^{-2}
300	11.2×10^{-2}	1.4×10^{-2}	12.2×10^{-2}	8.0×10^{-2}
350	11.9×10^{-2}	2.0×10^{-2}	15.9×10^{-2}	6.0×10^{-2}
400	14.8×10^{-2}	1.5×10^{-2}	14.3×10^{-2}	4.6×10^{-2}
Av values	10.7×10^{-2}	1.3×10^{-2}	12.9×10^{-2}	4.9×10^{-2}

[a] Intensity ratio: I_{3740}/I_{3640} (150°C).

particle sizes, employing both transmission and internal reflection techniques:

a. The intensity of the 3740 cm^{-1} band in transmission and internal reflection spectra should be higher for small particle size zeolites than for zeolite sample with larger particles, because the smaller particles have a larger external surface area.

b. The transmission and internal reflection spectra of the 0.4 μm zeolite should be almost identical concerning the intensity of the 3740 cm^{-1} band. In both methods the 0.4 μm particles are almost completely penetrated by the infrared light.

c. Only about 15% of the volume of the 1.9 μm zeolite particles are penetrated with the internal reflection method which scans preferably the region on or near the surface. The intensity of the 3740 cm^{-1} band should be therefore more intense for a given sample amount in internal reflection spectra than in the appropriate transmission spectra.

The results are summarized in Table 8. For the two NH_4-X zeolite samples the transmission and internal reflection spectra are identical concerning the number of O–H stretching bands, the corresponding band positions and the temperature dependency of the band intensities. Only the intensity of 3740 cm^{-1} band has different behavior (see Figs. 4 and 5). Because it is difficult to bring always exactly the same sample amount in contact with the internal reflection element or between the two transparent windows, we used the intensity of the strong band around 3640 cm^{-1} at 150°C as internal standard in both methods.

The intensities of the 3740 cm^{-1} band were normalized on the intensity of 3640 cm^{-1} band at 150°C by forming the ratio I_{3740}/I_{3640} (150°C). The temperature of 150°C was used because one can evaporate at 150°C most of the physically adsorbed water under high vacuum and the thermally instable lattice of the NH_4-X

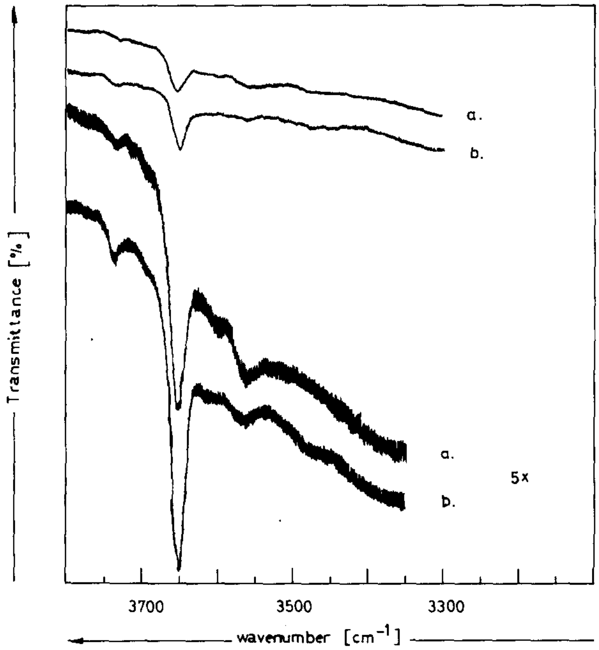

FIG. 4. Internal reflection spectra of NH_4-X zeolite. (a) 1.9 μm average particle size; (b) 0.4 μm average particle size.

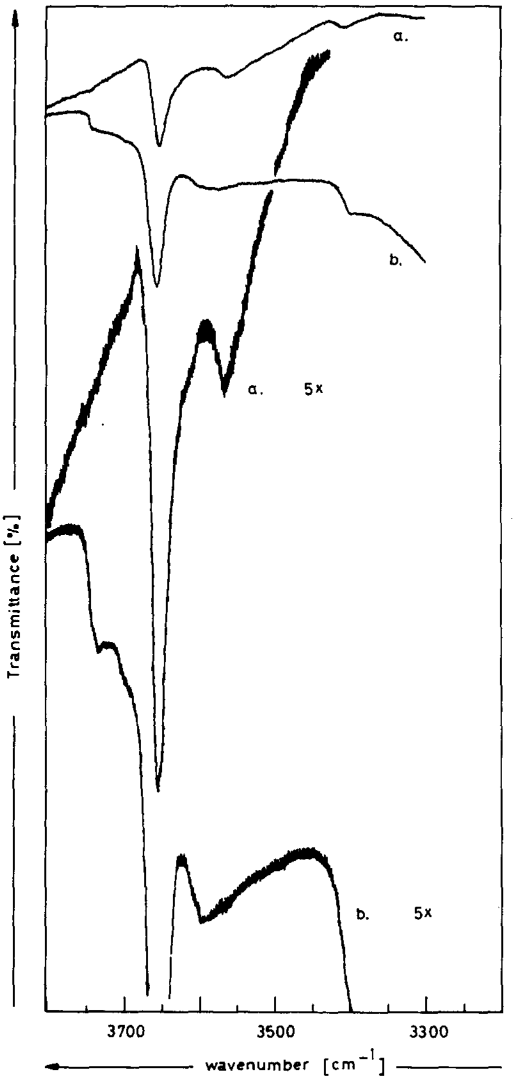

FIG. 5. Transmission spectra (powder) of NH_4-X zeolite. (a) 1.9 μm average particle size; (b) 0.4 μm average particle size.

zeolites is not yet destroyed. Table 8 shows the intensity ratios 3740/3640 (150°C) for different temperatures and the corresponding average values evaluated from transmission and internal reflection spectra. The intensity of the standardized 3740 cm^{-1} band in the internal reflection spectra of the 0.4 μm X-zeolite is much higher than the corresponding band intensity of 1.9 μm X-zeolite (see Table 8). The appropriate transmission spectra show even a more distinctive difference (see Table 8). These results lend therefore mild support for terminal OH groups. For the 0.4 μm particle size zeolite the intensity of the 3740 cm^{-1} band in both internal reflection and transmission spectra are fairly identical. The larger zeolite particles (1.9 μm) give rise to extensive intensity differences in internal reflection and transmission spectra. The normalized band at 3740 cm^{-1} shows in the internal reflection spectra a much higher intensity than in the appropriate transmission spectra. The intensity of the 3740 cm^{-1} band in transmission spectra is frequently as low as on the noise level. The ratios given in Table 8 for the transmission spectra of the 1.9 μm NH_4-X zeolite particle represent mostly the upper limit.

These data for small and larger NH_4-X zeolite particles from internal reflection and transmission spectra give more evidence to assign the 3740 cm^{-1} band to lattice terminating O–H groups.

The other possible assignment discussed in the literature is to correlate the 3740 cm^{-1} band to occluded silica impurities. If this band is due to silica impurities, then the less crystalline zeolite should have the more intense band. Adsorption measurements for the NH_4-X zeolites with 0.4 and 1.9 μm average particle diameter give a specific surface area of 1200 and 1010 m^2/g, respectively. It seems that the 1.9 μm particle size zeolite is less crystalline, because occluded amorphous silica lowers the specific surface area. The infrared spectra should show a more intense band, if the assignment to occluded silica is right. The obtained data, however, reveal the reverse result. No support can there be given for a correlation of the 3740 cm^{-1} band to occluded amorphous silica.

CONCLUSIONS

Because most OH groups of zeolites are located on the internal surface and shielded by the rigid zeolitic framework no influence of the pelletizing pressure on the frequency of the O–H band at 3640 cm^{-1} was observed up to 7000 kp/cm^2 for CaY and NH_4-Y zeolites. Between internal reflection and transmission spectra of X and Y zeolites no difference is observable concerning the band positions of the O–H stretching vibrations. But the intensities of the appropriate absorption bands are much higher in transmission than in internal reflection spectra, because of the different sample amounts interacting with the infrared light. The different intensities of the normalized band at 3740 cm^{-1} in internal reflection and transmission spectra of a NH_4-X zeolite with 0.4 and 1.9 μm particle sizes support the assignment of this band to lattice terminating OH groups.

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