Acetaldehyde adsorption on HZSM-5 studied by infrared spectroscopy

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The adsorption of acetaldehyde on HZSM-5 ($SiO_2/Al_2O_3 = 36$) at 313 K was examined using transmission infrared spectroscopy in the 4000–1300 cm^{-1} range. The structural hydroxyl groups of the zeolite were investigated and characterized by pyridine adsorption after the activation treatment (4 h in vacuum at 753 K). It was found that 94% of the acid sites are Brönsted centers. The spectra of acetaldehyde adsorbed at low pressures (2–3 Torr) indicate the proton transfer (by decreasing of the i.r. band at 3600 cm^{-1}) and the crotonaldehyde formation by aldol condensation followed by dehydration. However, the adsorption of acetaldehyde at pressures higher than 3 Torr shows the presence of oligomers by polymerization reactions.

Keywords: Acetaldehyde; HZSM-5; adsorption; aldol condensation; i.r. spectroscopy

INTRODUCTION

Zeolite HZSM-5 has been extensively studied since it was synthesized in the early 1970s.[1] Most of the investigations have concentrated on low molecular weight alcohols, methanol in particular, due to interest in the MTG process. However, the reactions of aldehydes, ketones, and other carbonyl compounds have received relatively little attention.

Chang and Silvestri[2] published a pioneer work about oxygenated hydrocarbon conversion on HZSM-5. Condensation reactions were proposed for the decomposition of two Fischer–Tropsh (F–T) model compounds on ZSM-5.[3] These F–T liquids contain about 10% of oxygenated hydrocarbons, including aldehydes and ketones, whose conversion to hydrocarbons increases the gasoline yield.

A new horizon is appearing in the organic chemistry for selective synthesis of intermediates using pentasil zeolites[4] involving isomerization, dehydration, aldol condensation, and other reactions with carbonyl compounds, mainly, aldehydes and ketones.

The use of i.r. spectroscopy as a tool to analyze the interaction of adsorbed molecules on ZSM-5 has been circumscribed to alcohols,[5,6] olefins,[7–9] and water.[10,11] We have embarked on a work to examine the interaction between the zeolite surface and aldehydes and ketones. The behavior of acetaldehyde in the adsorption pressure range 2–700 Torr using i.r. spectroscopy is shown in this paper.

EXPERIMENTAL

Zeolite preparation and characterization

ZSM-5 was synthesized in our laboratory using 1-propanol as template. The general directions to prepare the zeolite were based on several papers[12–14] following the hydrothermal method. We adopted a procedure as follows: A gel was obtained pouring two aqueous solutions into water. Solution 1 was sodium silicate (Riedel de Haen, 63% SiO_2, 18% Na_2O, and 18% H_2O) in water. Solution 2 was aluminum sulfate (Mallinckrodt), 1-propanol (Merck), and sulfuric acid (Cicarelli) in water. Vigorous mechanical stirring was used for homogeneous gel formation. The crystallization was performed in a stainless-steel reactor (Parr S4600 SS316, 1000 ml volume) at 453 K for 48 h at autogenous pressure.

The initial composition was $SiO_2/Al_2O_3 = 50$ $Na_2O/SiO_2 = 0.06$ and $H_2O/SiO_2 = 43$ (molar ratio). The zeolite obtained was analyzed by X-ray diffraction and i.r. spectroscopy for crystallinity, by SEM–TEM for morphology, and by atomic absorption for chemical composition.

The X-ray powder diffraction pattern of the sample was recorded using a Philips PW 1710 diffractometer with monochromatic CuKα radiation. The spectra of i.r. were recorded on a Perkin-Elmer 683 spectrophotometer equipped with a data station. The morphology was investigated using a Jeol JSM 35 Cf for SEM and a Jeol CXII for TEM. The chemical composition (Al and Na) was examined using a Perkin-Elmer 303 spectrometer.

Hydroxyl groups

The zeolite (Na form as-made) was transformed

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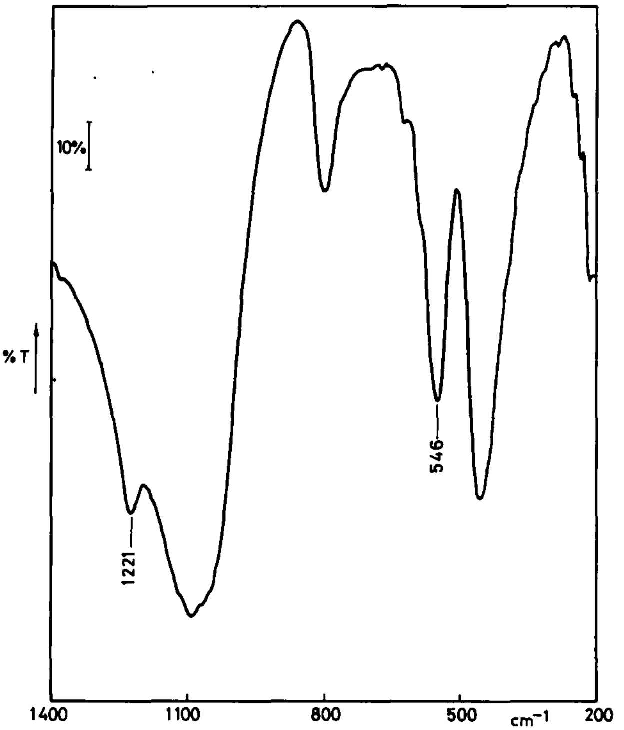


Figure 1 Framework i.r. region of our sample (KBr pellet technique).

into the ammonium form by an exchange in 1 M NH_4Cl solution. The exchange was carried out at 353 K and repeated several times until no signal of Na examined by atomic absorption was observed. For the i.r. spectroscopic studies, the zeolite was pressed into thin self-supporting wafers (10–15 mg/cm^2). The wafer inserted into the i.r. cell was pretreated *in vacuo* at 753 K for 4 h. Such treatment conditions were chosen on the basis of our experimental results. Under these conditions, decomposition of the NH_4^+ form and desorption of water took place without any appreciable dehydroxylation as is shown later by pyridine adsorption. DZSM-5 was prepared by exposing HZSM-5 to D_2O, followed by evacuation at 313 K.

The spectra were scanned 20 times to enhance the ratio signal/noise. The i.r. cell (KRS-5 windows) and the vacuum system were conventional. The temperature in all cases was measured using chromel–alumel thermocouple attached to the i.r. cell.

Pyridine adsorption

The zeolite sample (activated at 753 K *in vacuo*) was exposed to pyridine vapor (8 Torr, Merck) for 2 min at 313 K. Several spectra were recorded at different times of evacuation from 1800 to 1300 cm^{-1}. Finally, after 1 h of evacuation, the temperature was increased up to 423 K *in vacuo* to ensure the remotion of weakly adsorbed pyridine. A spectrum was registered with the chemisorbed pyridine at 313 K in the above range.

Acetaldehyde adsorption

The thin wafer of pure activated zeolite was exposed to acetaldehyde vapor (Riedel de Haen) at various adsorption pressures: 2, 6, 15, and 700 Torr at 313 K. Poor transmission was observed in the stretching region (C–H stretching). All spectra are shown between 1800 and 1300 cm^{-1}. These spectra at a particular adsorption pressure were recorded at various times of evacuation.

Crotonaldehyde adsorption

Our experimental results with acetaldehyde led us to investigate the crotonaldehyde adsorption. In this case, the activated zeolite was exposed to 1 and 4 Torr of crotonaldehyde vapors (BDH) at 313 K. After each adsorption, the system was evacuated for 1 h and the spectra were recorded in the bending region. In all cases, the behavior of the hydroxyl stretching band was analyzed.

RESULTS

Characterization of the zeolite

Figure 1 shows the i.r. spectrum of the framework absorption region (1400–200 cm^{-1}) of the sample using the KBr pellet technique. Assignments of the principal i.r. bands in this zone are shown in *Table 1*.[15,16] The band at 550 cm^{-1} is considered to be a good probe for detecting the presence of ZSM-5 zeolite framework.[13,17] The optical density (or absorbance ratio) of the 550 and 450 cm^{-1} bands is a characteristic parameter of crystallinity. For well-crystallized calcined ZSM-5 samples, this parameter is between 0.7 and 0.8.[13,17] Our calcined sample (filtered, washed, exchanged, and calcined in static air at 814 K) gave us a value of 0.73. *Table 2* shows the data of the XRD peaks in good agreement with literature values.[1,16,18] The degree of crystallinity was calculated following both the summation method proposed by Derouane et al.[19] and the method proposed by Jacobs[20] that consists in the sum of the area of the typical diffraction peaks between $2\theta = 22°$ and $25°$. Our calculated values of crystallinity were higher than 96% by both methods. The zeolite obtained consists typically of aggregates of coffin-lid crystals as revealed by SEM–TEM techniques.

The molecular formula (H form) deduced from chemical analyses was $(SiO_2)_{91.02}\ (AlO_2)_{4.97}Na_{0.32}\ H_{4.65}\cdot 24\ H_2O$, considering 96 atoms per unit cell.[21] Water content was determined by t.g.a., raising the temperature of calcination up to 1310 K. Aluminum percentage was 2.16 (4.08% as Al_2O_3) and SiO_2/Al_2O_3 was 36%.

Table 1 Vibration fréquencies for calcined HZSM-5

Wavenumber (cm^{-1})	Assignment[15–17]
448	$Si(Al)0_4$ bending
546	Distorbed double 5-rings
580	External link complex 5-membered ring
625	External link complex 5-membered ring
798	$Si(Al)0_4$ symmetric stretching
1095	$Si(Al)0_4$ asymmetric stretching
1221	Asymmetric stretching mode of 5-membered ring

Table 2 Comparison of XRD patterns

d[16]	I/I_{max}	d[1]	R.I.	d[a]	I/I_{max}	hkl[18]
11.16	52	11.1 ± 0.2	s	11.24	31	101
11.14	48					
10.05	29	10.0 ± 0.2	s	10.075	21	200
9.97	35					
9.743	24			9.772	5	
8.974	5					
7.461	3	7.4 ± 0.15	w	7.489	2	121
7.438	9					
7.079	6	7.1 ± 0.15	w	7.118	1	002
6.714	6					
6.368	17	6.3 ± 0.1	w	6.4	7	102
6.066	7	6.04 ± 0.1	w	6.01	10	301
5.994	11	5.97 ± 0.1	w			
5.959	5					
5.713	11			5.743	7	131
5.582	6					
5.570	5	5.56 ± 0.1	w	5.597	8	202
5.545	3					
5.376	2			5.392	2	122
5.367	3					
5.138	3					
5.024	3	5.01 ± 0.1	w	5.019	5	400
4.987	6					
4.614	7	4.6 ± 0.08	w	4.63	5	411
4.599	3					
4.452	2					
4.367	13			4.383	8	103
4.276	3					
4.268	3					
4.256	8	4.25 ± 0.08	w	4.277	10	421
4.089	3			4.099	3	203
4.009	7			4.021	7	402
4.002	2					
3.861	4					
3.850	100	3.85 ± 0.07	v.s.	3.866	100	501
3.841	2					
3.825	78			3.83	63	
3.757	37			3.766	39	
3.722	54	3.71 ± 0.05	s	3.729	43	303
3.713	5					
3.708	2					
3.651	40			3.66	30	133
3.487	3			3.499	7	
3.442	13			3.453	10	432
3.357	2			3.36	12	104
3.349	2					
3.342	4					
3.311	9			3.32	11	
3.053	12	3.04 ± 0.03	w	3.06	14	224
		2.99 ± 0.02	w	3.00	15	602
		2.94 ± 0.02	w	2.98	16	503

d: spacings *hkl*: planes v.s.: 60–100; s: 40–60; w: 10–20
[a] This work

OH groups

Figure 2a shows the i.r. spectrum of activated HZSM-5 in the 4000–3200 cm^{-1} range. A band at 3600 cm^{-1} and two weak bands at 3660 and at 3715 cm^{-1} were observed. Several experiments were carried out to select an appropriate temperature of activation for water remotion without dehydroxylation.

Figure 2b shows DZSM-5 after removing the exceeding D$_2$O. The OD band appears at 2658 cm^{-1} with two weak bands at 2700 and 2740 cm^{-1}.

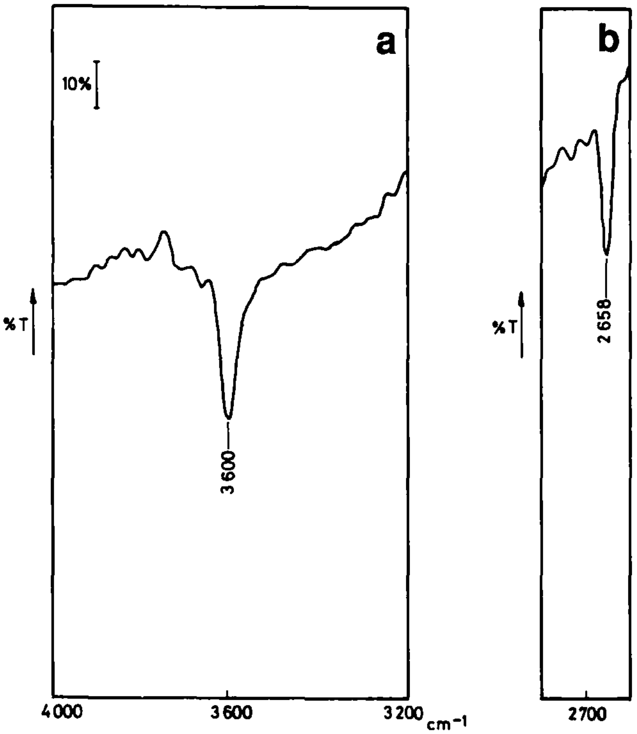


Figure 2 Hydroxyl groups after 4 h *in vacuo* at 753 K: (a) hydroxyl groups; (b) OD groups.

Pyridine adsorption

Adsorption of pyridine on HZSM-5 zeolite results in the appearance of the characteristic i.r. bands of the following complexes: PyH$^+$ ions at 1545 cm^{-1}, PyL (Lewis sites) at 1450 cm^{-1}, and PyNa$^+$ at 1445 cm^{-1}. Other bands appear at 1636, 1621, 1490, 1396, and 1338 cm^{-1}. The 1490 cm^{-1} band is not as useful for identification since it is common to Lewis and Brönsted species. *Figure 3* shows the subtraction spectrum between adsorbed pyridine and clean HZSM-5 in the 1800–1300 cm^{-1} region. This spectrum was recorded for chemisorbed pyridine at 313 K (after 1 h of evacuation at 423 K).

To obtain the Brönsted and Lewis acid-site concentration, the areas of the peaks at 1546 and 1450 cm^{-1} were calculated. The extinction coefficient values were taken from those proposed by Datka and Tuznik,[22] which are 0.058 cm^2 μmol^{-1} for PyH$^+$ and 0.084 cm^2 μmol^{-1} for PyL. We found that 94% of acid centers are of the Brönsted type; this means that only 0.3 from 4.97 Al per unit cell would be Lewis sites. Acidity of our sample, therefore, was predominantly of the Brönsted type without any appreciable dehydroxylation (see *Figure 3*). Consequently, the formation of Lewis sites is almost negligible.

Acetaldehyde adsorption

Several adsorptions were carried out on activated HZSM-5 using different pressures of acetaldehyde vapor at 313 K. Two features were found: At pressures lower than 3 Torr, the behavior of acetaldehyde could be studied since the spectra at various times of evacuation appear susceptible to analysis. On the

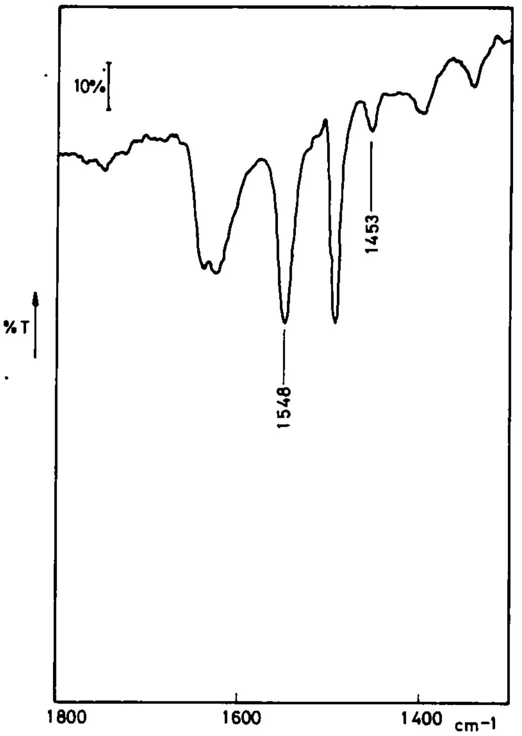


Figure 3 Subtraction spectrum for adsorbed pyridine recorded at 313 K after heating *in vacuo* at 423 K for 1 h.

other hand, at pressures higher than above, i.e., at 6, 15, and 700 Torr, the i.r. bands became broad and unclear in the bending region. We attribute this result to the formation of conjugated double bonds due to multiple condensation reactions. The stretching region in all cases was particularly troublesome because of the background noise; consequently, our information in this zone is not presented in this paper. All spectra were recorded between 1800 and 1300 cm^{-1}. The stretching vibration of the hydroxyl band located at 3600 cm^{-1} could be observed and analyzed.

Figure 4 shows the adsorption spectra for 2 Torr of acetaldehyde at 313 K after 5, 15, 30, 45, and 60 min of evacuation. These spectra are subtraction ones between the adsorbed acetaldehyde and the clean zeolite. Two bands were observed that reduce their intensity, evidencing their remotion from the zeolite surface. These bands at 1703 and at 1682 cm^{-1} are assigned to stretching vibration of the C=O group of two different species. *Table 3* shows the sequence and the possible assignment of the i.r. bands observed in the spectra. In this table, the i.r. bands of adsorbed acetaldehyde and pure liquid acetaldehyde are compared.

After 1 h of evacuation, the spectrum shows the remaining species on the surface and a longer time of evacuation does not change the i.r. pattern of the adsorbate. The most intense band of the spectrum is at 1630 cm^{-1} and a second band appears at approximately 1597 cm^{-1}. In our opinion, these bands are C=O stretching vibrations strongly interacting with the surface of the zeolite and C=C conjugated with the carbonyl group, respectively. The i.r. band at 1356 cm^{-1} reduces its intensity in a similar form to the bands at 1703 and 1682 cm^{-1}. Assignment in this zone is difficult to do, but it could be the deformation of the methyl group attached to a carbonyl group. The other bands are located at 1397 and 1430 cm^{-1}. The 1397 cm^{-1} band is the dominant in this part of the spectrum (1500–1300 cm^{-1}) for the remaining species. A weak band is observable at 1540 cm^{-1}.

Figure 5 shows the spectrum of the readsorption (6 Torr) of acetaldehyde on the same zeolite sample with the chemisorbed species. A broad band appears practically from 1700 to 1300 cm^{-1}. This band shows a maximum at 1550 cm^{-1} and bands at 1400, 1450, and 1515 cm^{-1} as well as shoulders at 1600 and 1630 cm^{-1}. This kind of spectrum was found by adsorption on recently activated HZSM-5 working with pressures higher than 3 Torr. This fact shows the reactivity of the acetaldehyde molecule for condensation reactions on the acid zeolite surface by forming possibly multiple conjugated systems. In all cases, the 3600 cm^{-1} band disappears completely after adsorption was finished.

Crotonaldehyde adsorption

The adsorption of crotonaldehyde was carried out on freshly activated HZSM-5 samples with pressures of 1 and 4 Torr at 313 K. The i.r. spectrum of 1 Torr of adsorbed crotonaldehyde is shown in *Figure 6*. This spectrum is a subtraction one from adsorbed crotonaldehyde and the clean zeolite after 30 min of evacuation. The main i.r. bands are at 1630 and 1602 cm^{-1}. A shoulder is observed at 1660 cm^{-1}, which is attri-

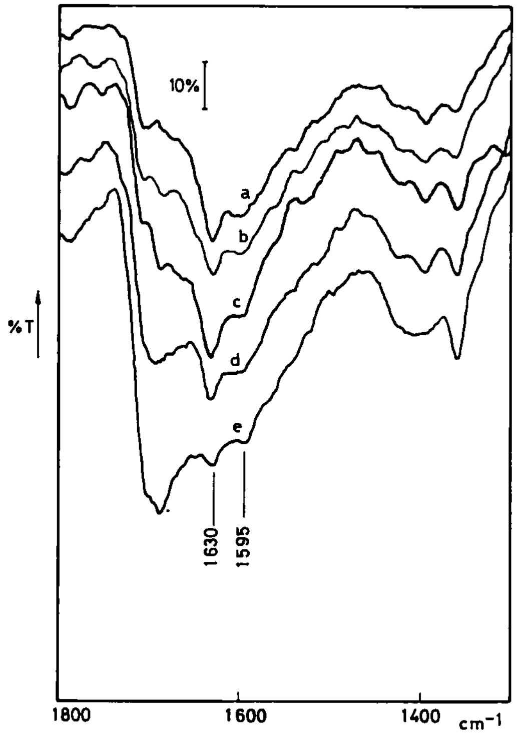


Figure 4 Subtraction spectra for adsorbed acetaldehyde (2 Torr): (a) 60 min of evacuation; (b) 45 min; (c) 30 min; (d) 15 min; (e) 5 min.

Table 3 Comparison between adsorbed and liquid acetaldehyde in the 1800–1300 cm^{-1} range

	Adsorbed (2 Torr) evacuation times (min)						
Liquid	5	15	30	45	60	Readsorbed (6 Torr)	Assignment
1725			1707	1704	1703		νC=O
		1694					
	1686		1686	1683	1680		νC=O
	1630	1632	1630	1630	1630	1630	νC=O
	1594	1601	1597	1597	1602		νC=C
						1575	
						1550	
						1540	
						1515	
						1450	
1446	1420	1430	1430	1430	1430		δ_{as} CH
1415	1397	1397	1397	1397	1397	1400	δ_s CH
1342	1359	1360	1360	1360	1360	1365	

buted to stretching vibration of carbonyl group interacting with hydrogen bond that reduces its frequency in 20 cm^{-1} in respect to the stretching vibration of the carbonyl group of liquid crotonaldehyde (1680 cm^{-1}). The rest of the bands are vibrating at ~ 1430, 1400, and 1360 cm^{-1} (shoulder).

This adsorption i.r. pattern is almost identical to that obtained with adsorbed acetaldehyde using a little amount of adsorbate. The behavior of crotonaldehyde at adsorption pressures higher than 1 Torr evidences again the occurrence of polymerization reactions resulting in the appearance of broad bands in the i.r. bending region. *Table 4* compares i.r. bands of pure liquid crotonaldehyde with adsorbed (1 Torr) crotonaldehyde.

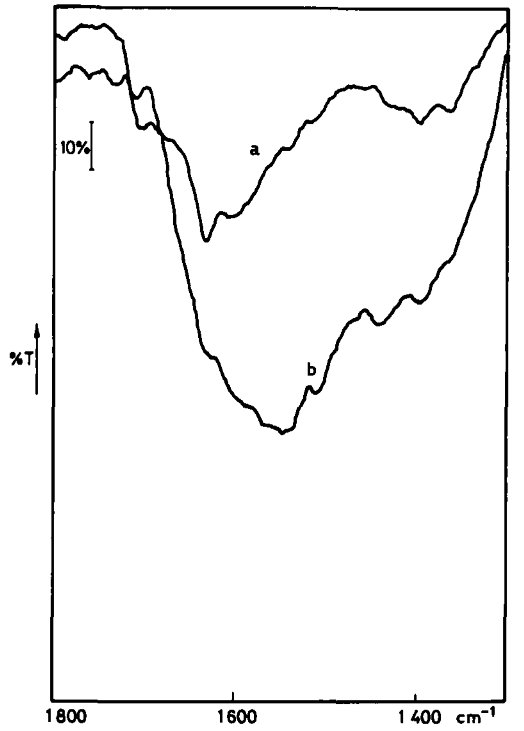


Figure 5 Subtraction spectra for (a) adsorbed acetaldehyde after 60 min of evacuation and (b) readsorbed acetaldehyde (6 Torr) after 30 min of evacuation.

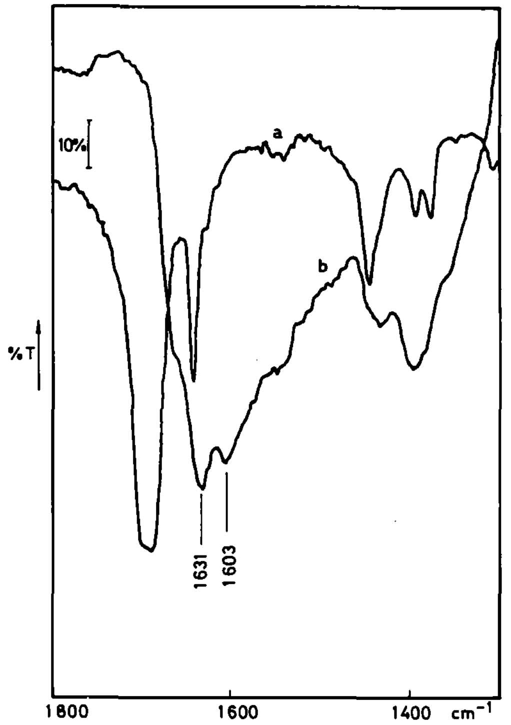


Figure 6 (a) Liquid crotonaldehyde; (b) subtraction spectrum for adsorbed crotonaldehyde after 30 min of evacuation.

DISCUSSION

OH groups and pyridine adsorption

To choose an appropriate temperature of activation and to know the nature of acid centers under these conditions, the hydroxyl groups were investigated at different temperatures under *vacuo*. On the basis of previous data[23–25] and from our experimental results, a temperature of 753 K was chosen as the activation temperature for all ZSM-5 samples.

Acidity of zeolitic materials has been widely studied since the major applications of zeolites in heterogeneous catalysis result from their acidic properties. Several techniques have been used for these studies: i.r. spectroscopy, microcalorimetry, temperature-programmed desorption, and electron spin resonance.[23–25] Auroux et al.[23] and Vedrine et al.[24]

Table 4 I.r. bands of adsorbed and liquid crotonaldehyde (1800–1300 cm^{-1})

Liquid	Adsorbed	Assignment
1690		νC = O
	1660	νC = O
1640		C = C
	1630	νC = O
	1602	C = C
1442	1442	
1392	1395	δ CH
1375	1360	

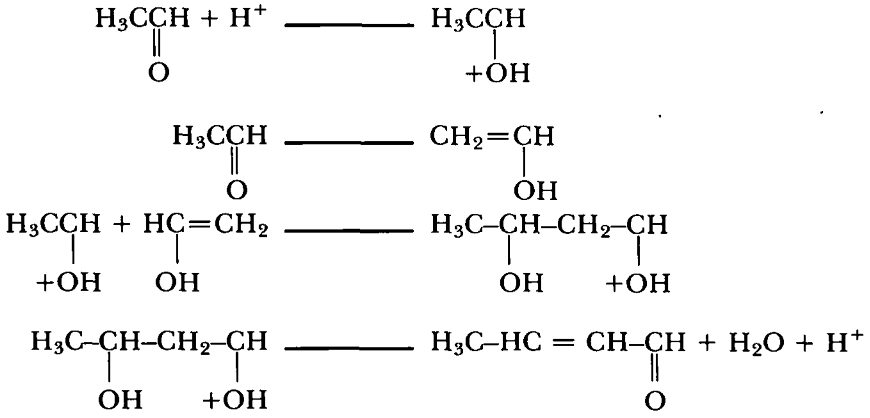
reported i.r. absorption bands at 3720 and 3605 cm^{-1} with a shoulder at 3665 cm^{-1}. The band at 3605 cm^{-1} has been assigned to Brönsted acid centers, and the band at 3720 cm^{-1}, to silanol groups. The maximum intensity of the i.r. bands has been observed by these authors at temperatures between 635 and 685 K. Above this temperature, dehydroxylation occurred with a subsequent decrease of the hydroxyl bands in the stretching region.[24] However, we observed well-resolved i.r. bands at 753 K after 4 h of evacuation under 10^{-3} Torr without any appreciable dehydroxylation, which was corroborated by pyridine adsorption. .The i.r. spectrum of our sample presents an absorption band at 3600 cm^{-1} with two weak bands at 3660 and 3715 cm^{-1}. Our results are in agreement with the values of i.r. bands cited in the literature.[23–25] Jacobs and von Ballmoos[26] pointed out that for highly crystalline zeolites (defect-free) HZSM-5, the only band should be the band at 3610 cm^{-1}. The band at 3740 cm^{-1} (reported sometimes at 3720 cm^{-1}) was found to decrease with increasing crystallinity of the samples.[27] Datka and Piwowarska[28] suggested that weak Brönsted acid centers could be vibrating at 3670 cm^{-1}. Our results, as can be seen in *Figure 2a*, are consistent with samples of good crystallinity.

Pyridine adsorption has been used extensively to characterize acid centers of HZSM-5 zeolites.[22–25,28] At 753 K and 10^{-3} Torr, our results reveal dominant Brönsted sites and a low concentration of Lewis sites.

Acetaldehyde adsorption

I.r. spectroscopy has been used by investigators to study the adsorption of acetaldehyde on several surfaces such as silica–gel, magnesium oxide, tin oxide, hematite, or silica–alumina.[29–31] Assignments of bands in the i.r. spectra of the zeolite surface under *in situ* reaction conditions are complicated; however, by comparison of spectra, some species could be identified using some reasonable arguments. The absorbed acetaldehyde at low adsorbate pressures indicate the probable formation of crotonaldehyde or, eventually, the products of additional condensation reactions of crotonaldehyde.

The mechanism for acid-catalyzed aldol condensation is[32]:



$$H_3C\underset{\underset{O}{\|}}{C}H + H^+ \;\rule[0.5ex]{3em}{0.4pt}\; H_3C\underset{\underset{+OH}{|}}{C}H$$

$$H_3C\underset{\underset{O}{\|}}{C}H \;\rule[0.5ex]{3em}{0.4pt}\; CH_2{=}\underset{\underset{OH}{|}}{C}H$$

$$H_3C\underset{\underset{+OH}{|}}{C}H + H\underset{\underset{OH}{|}}{C}{=}CH_2 \;\rule[0.5ex]{3em}{0.4pt}\; H_3C{-}\underset{\underset{OH}{|}}{C}H{-}CH_2{-}\underset{\underset{+OH}{|}}{C}H$$

$$H_3C{-}\underset{\underset{OH}{|}}{C}H{-}CH_2{-}\underset{\underset{+OH}{|}}{C}H \;\rule[0.5ex]{3em}{0.4pt}\; H_3C{-}HC = CH{-}\underset{\underset{O}{\|}}{C}H + H_2O + H^+$$

Dehydration is a fast path for acid catalysis. Intermediate acetaldol is not easy to identify although it could be stabilized on the zeolite surface. Physically adsorbed acetaldehyde is represented by two vibrational bands at 1703 and 1360 cm^{-1} (see *Figure 4*). The former is probably a C=O stretching vibration interacting with surface hydroxyl groups, and the second band, a deformation vibration related to weakly adsorbed acetaldehyde. These bands are easily removed from the zeolite surface. In addition, two bands remained with constant intensity at 1630 and 1597 cm^{-1}. The band at 1630 cm^{-1} could be assigned to a C=C stretching vibration, to a bending mode of adsorbed water, or to a C=O vibration strongly interacting with the surface of the zeolite. Adsorption of crotonaldehyde shows an i.r. spectrum very similar to that of acetaldehyde, both at low adsorption pressures. This fact evidences that the band at 1630 cm^{-1} is probably a carbonyl stretching vibration of chemisorbed crotonaldehyde and the band at ~ 1600 cm^{-1}, a C=C vibration conjugated to the C=O group. Using high adsorbate pressures (acetaldehyde or crotonaldehyde), the spectra show oligomeric species represented mainly by i.r. bands in the range from 1600 to 1450 cm^{-1}. Additionally, a gray color was observed in the disk of zeolite after adsorption with increasing pressures of adsorbate was performed.

CONCLUSIONS

- Primary interaction between acetaldehyde and the zeolite surface is proton transfer (band at 3600 cm^{-1} vanishes and the carbonyl vibration shifts to lower frequencies).
- Crotonaldehyde was identified as a product of aldol condensation or as an intermediate of additional condensation reactions (almost identical spectra for adsorbed crotonaldehyde in respect to adsorbed acetaldehyde are observed at low adsorption pressures).
- Relatively high adsorption pressures induce polymerization (broad bands appear in the bending region).
- HZSM-5 is strongly active for aldol condensation (i.e., for SiO_2/Al_2O_3 = 36 zeolite).
- I.r. technique, though useful, should be com-

plemented by other analytical techniques for a further study of intermediates on the zeolite surfaces.

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