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Adsorption and Reaction of Ethyne on Partially Zinc Exchanged Type A Zeolite: A FTIR Study

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The interaction of ethyne and ethyne-d_2 with ZnNa–A zeolite yields results very different from those reported for related systems. Two adsorbed ethyne complexes are observed. One, a stable side-on π-bonded species is formed by coordination with the Na^+ cations. The second has been identified as zinc acetylide ($Zn—C\equiv C—H$) and was observed to react slowly with zeolitic water to form ethanal. The rapid deuteration of hydroxyl groups and zeolitic water on adsorption of C_2D_2 was observed to be more efficient than exchange with D_2O. Adsorption of ethyne by Ag–A zeolite was reinvestigated and it is shown that ethanal is formed over periods of prolonged contact.

Introduction

Infrared spectroscopy has proven to be a useful method for studying the molecular level interactions that occur between adsorbate species and a catalyst surface. The nature of these interactions may be inferred from the changes which occur in the intramolecular vibrations of the adsorbate molecule on adsorption and bonding to the surface. These changes often result from a lowering of the molecular symmetry, leading to the observation of modes that are inactive in the free molecule. This has previously been illustrated in studies of molecules such as ethyne and ethene adsorbed on a variety of zeolites, where the IR inactive (in the gas phase) triple and double bond stretching vibrations were observed, indicating the formation of π-complexes with the zeolite cations.[1,2]

In this paper a study of the interaction of ethyne and ethyne-d_2 with partially Zn exchanged Na–A zeolite (ZnNa–A) by Fourier transform infrared (FTIR) spectroscopy is reported. The observation of both stable and reacting species reveals results very different from those previously reported for related systems.[2-6]

Previous studies of the interaction of C_2H_2 with zeolites have shown that four kinds of adsorption complexes may be envisaged: (1) "end-on" via interaction with the acidic protons of C_2H_2 and the framework oxygens,[7] (2) "side-on" via overlap of the π-orbitals of C_2H_2 and cation orbitals of the correct symmetry to form a π-complex,[2,5,6] (3) loss of one or both hydrogens to form acetylides,[6,8] and (4) reactions to form new species.[9] In all cases complex formation has a marked effect on the frequency of the ν_2 ($C\equiv C$) stretching vibrations.

In view of our findings on ZnNa–A we have also reinvestigated the adsorption of C_2H_2 by Ag_{12}–A (Ag–A) zeolite, where previously only stable species were identified.[2] A study was also made of Na–A zeolite to aid in the spectral assignments of the adsorbed species and is reported elsewhere.[10] The behavior of Ag–A was found to be similar to ZnNa–A, whereas in Na–A only stable species were identified.

Experimental Section

ZnNa–A zeolite was prepared by ion exchange of Linde-type Na–A powder (BDH) with a 0.1 M solution of $ZnCl_2$ for 7 days at room temperature. The volume of solution used contained the stoichiometrically correct quantity of Zn^{2+} ions required for the desired degree of ion exchange. Analysis by atomic adsorption spectroscopy gave the exact degree of ion exchange. Two samples of ZnNa–A zeolite were used in the present study, viz. sample 1, $Zn_{4.3}Na_{3.4}$–A (high exchange) and sample 2, $Zn_{1.1}Na_{9.8}$–A (low exchange). The Ag_{12}–A (Ag–A) zeolite investigated in the present work was obtained from the same batch used in the previous study of C_2H_2 adsorption.[2]

Ethyne (99%, British Industrial Gases Ltd.) was purified by passing the gas slowly through concentrated sulfuric acid, after which it was freeze–pumped–thawed before use. Ethyne-d_2 (99 atom % D, Merck, Sharp and Dohme Ltd.) was used without further purification.

Infrared measurements were made on thin self-supporting disks (ca. 7 mg cm^{-2}) of zeolite. These were pressed using a 1.5 cm diameter die to which a known mass of zeolite was added at a pressure of 6600–8400 kg cm^{-2}. Sample treatments (dehydrations, adsorption, etc.) were performed in an all-metal IR cell fitted with KRS-5 windows[11] which remained in the sample compartment of the spectrometer for the duration of the experiment. The cell was attached to an all-metal vacuum system, consisting of a turbomolecular pump backed by a rotary oil pump. Adsorbate pressures were measured with a transducer type gauge (Baratron). Zeolite samples were pretreated (dehydrated) by heating under vacuum to 700–750 K for 12–15 h (2 h at 673 K for Ag–A).

Infrared spectra were measured in transmission with a Nicolet 60SX FTIR spectrometer at a resolution of 2 cm^{-1}. A data collection time of 4 min (512 scans) was used unless otherwise stated. Use was made of data subtraction routines to remove bands due to water vapor. These resulted from the different concentrations of water vapor in the spectrometer during collection of the reference and sample spectra.

Results and Discussion

Following the adsorption of C_2H_2 or C_2D_2 by ZnNa–A (sample 1) at beam temperature, several new IR bands are observed (Figures 1 and 2). By comparison with previous studies these bands are assigned to *two* adsorbed complexes formed within the zeolite cavities by the interaction of C_2H_2 with the cations. With prolonged contact at ambient temperature one of the species is observed to react to form ethanal.

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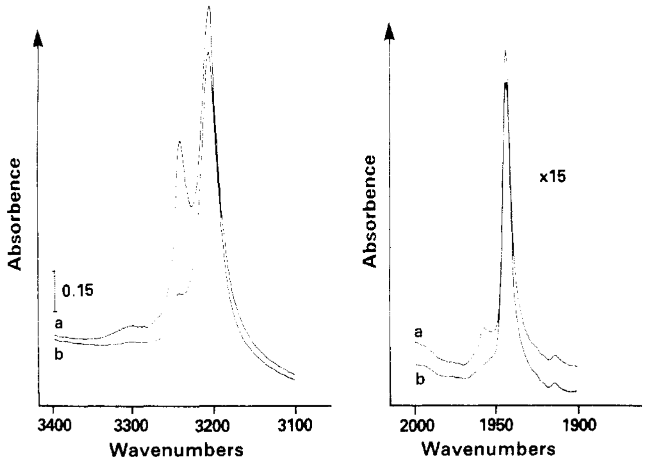

Figure 1. Effect of pressure on the spectrum of ethyne adsorbed on ZnNa–A zeolite: (a) zeolite + 10.7 Torr of C_2H_2; (b) zeolite + 1 Torr of C_2H_2.

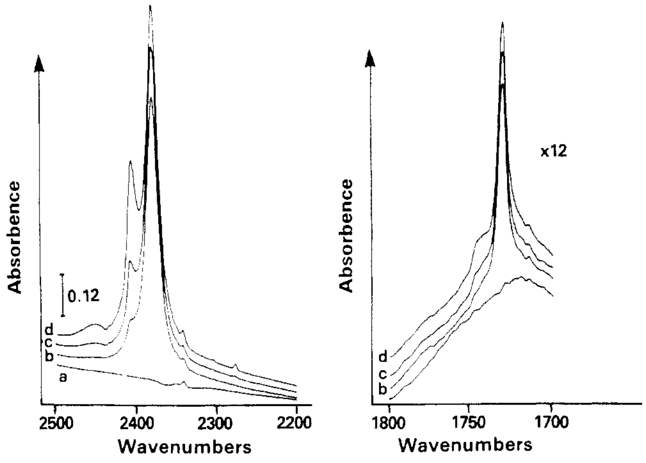

Figure 2. Effect of pressure on the spectrum of ethyne-d_2 adsorbed on ZnNa–A zeolite: (a) dehydrated zeolite background; (b) zeolite + 1.5 Torr of C_2D_2; (c) zeolite + 4.7 Torr of C_2D_2; (d) zeolite + 13.6 Torr of C_2D_2. Data collection time 64 s.

1. The Adsorption of C_2H_2 and C_2D_2 on ZnNa–A (Sample 1). The IR spectra of C_2H_2 and C_2D_2 adsorbed on ZnNa–A are depicted in Figures 1 and 2. For adsorbed C_2H_2 in the region 1900–2000 cm^{-1}, two bands of very different intensities are observed (Figure 1) at 1955 and 1943 cm^{-1}. These we assign to the $\nu(\mathrm{C{\equiv}C})$ stretching vibration (1974 cm^{-1} in the gas phase[12]) of two adsorbed ethynic complexes, A and B, respectively. Two bands are also observed in the region above 3000 cm^{-1}, at 3238 and 3203 cm^{-1}, which are due to $\nu(\mathrm{C{-}H})$ vibrations[12] of the adsorbate complexes. From a comparison of the changes in the relative intensities of the $\nu(\mathrm{C{-}H})$ and $\nu(\mathrm{C{\equiv}C})$ modes on increasing the C_2H_2 overpressure (Figure 1) and on evacuation of the gas phase (Figure 3), the bands at 3238 and 3203 cm^{-1} are assigned to species A and B, respectively. Above 1200 cm^{-1} an additional band is observed at 1366 cm^{-1} (Figure 3). Its assignment is not so clear as the other bands and is considered later. In the region below 1200 cm^{-1}, bands due to the adsorbed C_2H_2 complexes were observed at 763 and 750 cm^{-1}. These, from their pressure dependence, are assigned to $\delta(\mathrm{C{\equiv}C{-}H})$ of species A and species B, respectively. A summary of the band assignments are given in Table I.

In Figure 2 the spectra of C_2D_2 adsorbed on ZnNa–A are depicted. Two $\nu(\mathrm{C{\equiv}C})$ vibrations are observed at 1744 and 1731 cm^{-1} and two $\nu(\mathrm{C{-}H})$ vibrations at 2403 and 2378 cm^{-1}. The behavior of these bands on increasing the pressure and on evacuation, compared with the C_2H_2 data, allows the modes at 2403 and 1744 cm^{-1} to be assigned to species A, while those at 2378 and 1731 cm^{-1} are attributed to species B (Table I). The calculated isotopic shifts for the $\nu(\mathrm{C{-}H/D})$ and $\nu(\mathrm{C{\equiv}C})$ modes of the two adsorption complexes are identical with those observed in the gas phase.[12]

TABLE I: Summary of the Vibrational Bands (cm^{-1}) and Their Assignments for Ethyne and Ethyne-d_2 Adsorbed on ZnNa–A Zeolite Initially and after Prolonged Contact

C_2H_2		C_2D_2		
initial contact	prolonged contact	initial contact	prolonged contact	assignment
3238	3283	2403	2403	$\nu(\mathrm{C{-}H})/\nu(\mathrm{C{-}D})$ of π-bonded ethyne, species A
3203		2378		$\nu(\mathrm{C{-}H})/\nu(\mathrm{C{-}D})$ of zinc acetylide, species B
1955	1955	1744	1744	$\nu(\mathrm{C{\equiv}C})$ of π-bonded ethyne species A
1943		1731		$\nu(\mathrm{C{\equiv}C})$ of zinc acetylide, species B
			1715	$\nu(\mathrm{CO})$ of H-bonding ethanal
	1685		1666	$\nu(\mathrm{CO})$ of adsorbed ethanal
	1640		1606	$\delta(\mathrm{HOH})$ of zeolitic water
			1450 1410	$\delta(\mathrm{HOD})$ of zeolitic water
1366				zinc acetylide, unassigned
	1414 1355			$\delta(\mathrm{C{-}H})$ and $\delta(\mathrm{CH_3})$ of adsorbed ethanal
			1312	$\delta(\mathrm{C{-}H})/\delta(\mathrm{CH_3/CH_2D/CHD_2})$ of partially deuterated ethanal
736				$\delta(\mathrm{C{\equiv}C{-}H})$ of π-bonded ethyne, species A
750				$\delta(\mathrm{C{\equiv}C{-}H})$ of zinc acetylide, species B

The adsorption strengths of the complexes were investigated by adsorbing C_2H_2 (14.2 Torr) and immediately evacuating the sample cell. Spectra obtained as a function of evacuation time are shown in Figure 3. The data indicate that the bands at 3238 and 1955 cm^{-1} are immediately lost, while the remaining bands (3293, 1943, and 1366 cm^{-1}) decrease steadily in intensity over a period of 60 min. Clearly species A is due to a weakly adsorbed species, while species B is associated with a more strongly coordinated complex. From the behavior of the 1366-cm^{-1} band on evacuation it is reasonable to attribute this band to species B.

2. Identification of the Adsorption Complexes. Consider firstly the assignment of species A giving rise to bands at 3238, 1955, and 763 cm^{-1}. The observed $\nu(\mathrm{C{\equiv}C})$ vibration at 1955 cm^{-1} is typical of those observed for side-on π-bonded C_2H_2 complexes[2,5,6] and thus species A is assigned such a complex formed with either a Zn^{2+} or Na^+ cation. Previously it has been observed that, in ZnNa–A and other mixed cation zeolites, hydrocarbons such as propene may form complexes with one or both of the cations.[13] Later it will be shown that species A, unlike species B, does not react when left in contact with the zeolite for prolonged periods. We have previously observed C_2H_2 to form complexes with the Na^+ cation in Na–A zeolite.[10] This study showed that C_2H_2 adsorbed on Na–A does not react when left in prolonged contact with the zeolite and that $\nu(\mathrm{C{\equiv}C})$ of the π-bonded ethyne complexes were observed at 1954, 1950, and 1942 cm^{-1}. All of these values are very similar to those observed for species A in ZnNa–A. X-ray diffraction studies of ZnNa–A zeolite have shown that the Na^+ cations are located in the accessible S_I or $S_I{}^*$ sites.[14] Assuming this to be the case in our ion-exchanged zeolite, it is then not unreasonable that the Na^+ cations are able to interact with C_2H_2. Species A is thus assigned to weakly adsorbed C_2H_2 which forms a side-on π-bonded complex with the Na^+ ions in the α-cages.

The value of $\nu(\mathrm{C{\equiv}C})$ observed for species B (1943 cm^{-1}) also falls within the range 1960–1912 cm^{-1} associated with π-bonded C_2H_2. This does not, however, explain the band at 1366 cm^{-1}, which is clearly associated with this complex. No band has previously been reported for π-bonded C_2H_2 in this region, and

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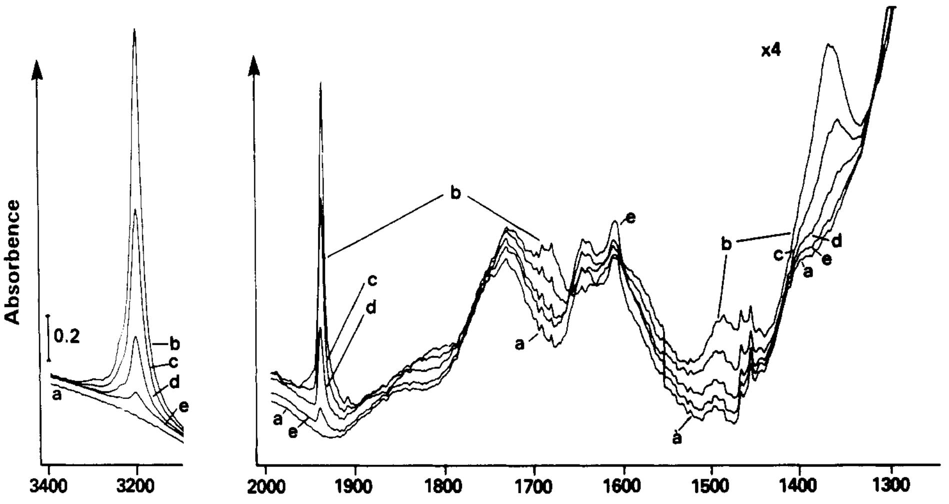

Figure 3. Evacuation of C_2H_2 (14.6 Torr) from ZnNa-A zeolite immediately after adsorption: (a) dehydrated zeolite background; (b) evacuation of C_2H_2 immediately after adsorption (16 s); (c) evacuation for 1.3 min (16 s); (d) Evacuation for 10 min (31 s); (e) evacuation for 1 h (64 s).

TABLE II: Comparison of the Vibrational Bands (cm^{-1}) of Species B with Those Reported for Zinc Acetylide Salts[15,16][a]

species B	$Zn(C\equiv C)_2\cdot 2NH_3$[b]	$K_2[Zn(C\equiv CH)_4]$[c]	assignt
3203	3236 (s)	3290 (s)	ν(C-H)
1943	1961 (w)	1940 (w)	$\nu(C\equiv C)$
1366		1370 (b,s)	unassigned
750		650-670 (w)	$\nu(C\equiv C-H)$

[a] s = strong, w = weak, b = broad. [b] Reference 15. [c] Reference 16.

thus it seems unlikely that species B is due to a π-bonding complex. Other possible complexes are end-on coordination, acetylide formation, or reaction to form a new product. New product formation can be discounted as both the ν(C-H) and $\nu(C\equiv C)$ are indicative of an ethynic type complex. For end-on adsorption $\nu(C\equiv C)$ has been reported at values greater than 1974 cm^{-1}; thus this can be discounted. The final possibility for species B is that it is due to an acetylide species. Comparison of the vibrational modes of species B with those reported for zinc acetylide salts[15,16] in Table II reveals a distinct similarity in both the wavenumber values and number of the vibrational modes observed. Although the species B bands do not completely agree with those of the acetylide complexes, some differences in the vibrational energies of an inorganic complex and one formed in a zeolite framework would clearly be expected considering the unique nature of the zeolite framework. We therefore assign species B to a strongly adsorbed zinc acetylide ($Zn-C\equiv C-H$) complex that is located in the α-cages.

Difference spectra of data before and after the adsorption of C_2H_2 reveal the loss of the hydroxyl bands present in the dehydrated zeolite. This indicates the interaction of the hydroxyl groups with the adsorbate and with H^+ released from the formation of zinc acetylide. The H^+ produced will also coordinate to zeolitic water present in the cavities forming hydronium (H_3O^+) ions. No spectroscopic evidence was found in the IR data for these ions.

3. Effect of Prolonged Contact Time on Adsorbed Ethyne. When gaseous C_2H_2 is left in contact with ZnNa-A (sample 1) the bands assigned to species B at 3203, 1943, and 750 cm^{-1} were found to decrease slowly in intensity, while the feature at 1366 cm^{-1} developed a shoulder and a new band appeared at 1685 cm^{-1}. Representative data collected over a period of 24 h are depicted in Figure 4. After 24 h all four bands associated with species B had disappeared, while the weaker bands associated with species A remained unchanged. On evacuating after 24 h contact (Figures 4 and 5) new bands are clearly visible at 1685, 1414, and 1355 cm^{-1}. The band at ca. 1642 cm^{-1} and the broad ν(OH) band above 3100 cm^{-1} are due to water readsorbed by the zeolite.

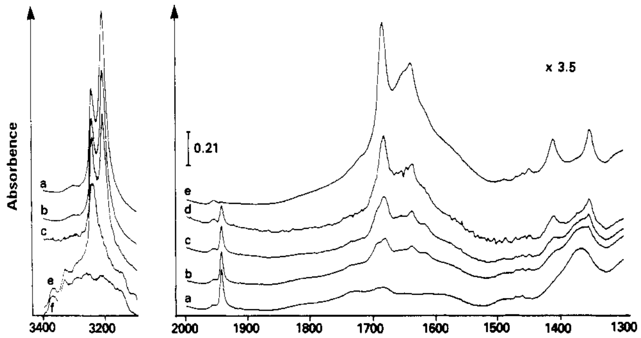

Figure 4. Effect of prolonged contact on the spectrum of C_2H_2 (8.5 Torr) adsorbed on ZnNa-A: (a) spectrum 3e after adsorption of 8.5 Torr C_2H_2; (b) after 5 h; (c) after 8 h; (d) after 13 h; (e) after 24 h; (f) 3400-3100-cm^{-1} region after evacuation of gas phase.

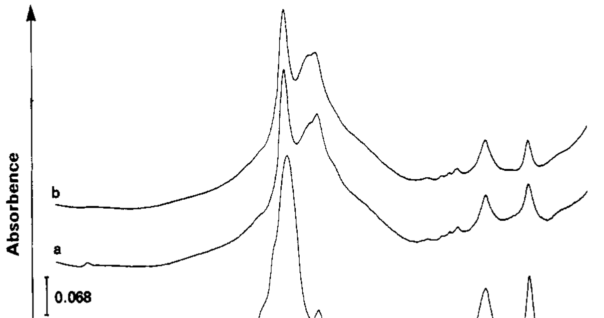

Figure 5. Identification of hydration product of ethyne on ZnNa-A zeolite: (a) ZnNa-A + C_2H_2 (8.5 Torr) after 24 h contact; (b) after evacuation on gas phase; (c) ZnNa-A + adsorbed ethanal.[17]

The new band at 1685 cm^{-1} is characteristic of ν(CO) stretching vibrations, suggesting that a carbonyl-containing species is the reaction product. The most likely route to such a product is via a hydration reaction of zinc acetylide (species B) with residual water or, more probably, H_3O^+ present in the zeolite cavities. The simplest hydration product of zinc acetylide is ethanal (CH_3CHO). Comparison of parts b and c of Figure 5 clearly shows that the bands due to adsorbed ethanal[17] coincide with those of the reaction product. We therefore assign the new bands observed at 1685,

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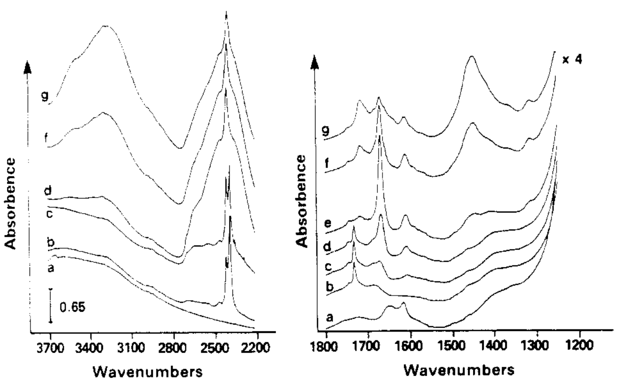

Figure 6. Effect of prolonged contact on the spectrum of C_2D_2 (16.8 Torr) adsorbed on ZnNa–A zeolite: (a) dehydrated zeolite background; (b) adsorption 16.8 Torr of C_2D_2; (c) after 30 min; (d) after 3 h; (e) after 8 h; (f) after 13 h; (g) after 18 h.

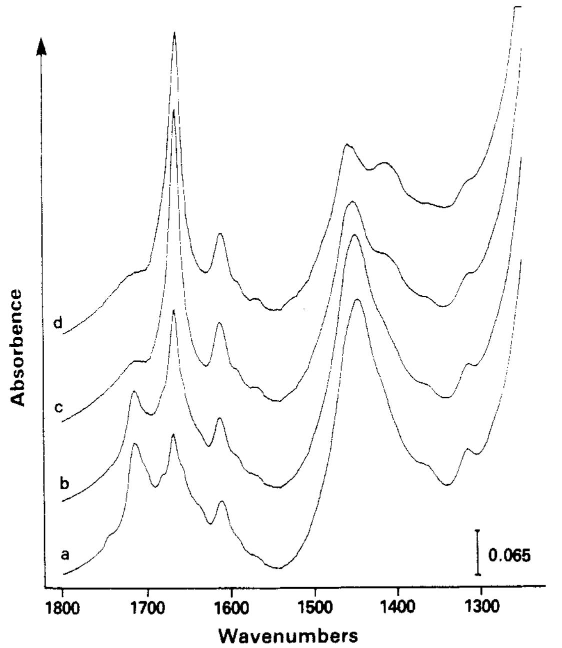

Figure 7. Evacuation of C_2D_2 from ZnNa–A zeolite after 18 h contact: (a) ZnNa–A + C_2D_2 after 18 h; (b) evacuation of sample; (c) evacuation for 10 min; (d) evacuation for 2 h.

TABLE III: A Summary of the Vibrational Bands (cm^{-1}) and Their Assignment for Ethyne Adsorbed on Ag–A Zeolite

zeolite background	initial adsorpn of C_2H_2	after 16 h contact	assignment
3610	3655 3584		ν(OH) of framework
3590–3000			ν(OH) of H-bonding water and OH
	3206 3171 (sh)		ν(CH) of adsorbed C_2H_2
		2500	$H_3O^+\cdot H_2O$
	1950 1912		$\nu(C{\equiv}C)$ of π-bonded C_2H_2
	1816		$\nu(C{\equiv}C)$ of $Ag{-}C{\equiv}C{-}H$
		1719 1684	ν(CO) of ethanal
1648	1652		δ(HOH)
		1415 1352 1314	$\delta(CH_3)$ and δ(CH) of ethanal

1414, and 1355 cm^{-1} to an Zn–ethanal adsorption complex. Band assignments are summarized in Table I. Further details of the adsorption of ethanal by ZnNa–A are given elsewhere.[17]

The hydration of C_2D_2 on ZnNa–A (sample 1) was also followed over periods of prolonged contact. Representative spectra obtained over an 18-h period are depicted in Figure 6 and summarized in Table I. The data show that bands due to species A remained unchanged, while those associated with species B disappeared as ethanal was formed. As the hydration reaction occurred between C_2D_2 and H_2O, the ethanal formed will be partially deuterated. The ν(CO) band of the partially deuterated ethanal was first observed at 1666 cm^{-1}. With increased contact time the intensity of this band decreased as a new ν(CO) vibration appeared at 1715 cm^{-1}. On evacuating the sample after 18 h (Figure 7) the intensity of the 1666-cm^{-1} band was restored at the expense of the 1715-cm^{-1} band. The appearance of the second ν(CO) band coincided with an increase in the intensity of the bands due to adsorbed zeolitic water, while its disappearance on evacuation paralleled the removal of zeolitic water from the cavities. The 1715-cm^{-1} band thus appears to be associated with ethanal that is weakly hydrogen bonding to zeolitic water.[17] The 1666-cm^{-1} band is assigned to ethanal coordinating to the Zn^{2+} cations. The observation of only one ethanal species with C_2H_2 was probably associated with the much smaller quantity of water readsorbed by this zeolite sample during the reaction time. A deformation and/or bending mode of the partially deuterated CH_3 and C–H groups is observed at 1312 cm^{-1} (Figure 6e). The other deformation modes will be shifted to below 1250 cm^{-1} due to their partial deuteration and are hence obscured by the intense framework vibrations.

The readsorption of water by the zeolite in the C_2D_2 experiment (Figure 6) is seen by the appearance of hydroxyl bands in the 3650–3100-cm^{-1} (ν(OH)) and 2700–2200-cm^{-1} (ν(OD)) regions and the deformation modes of HOD at 1450 and 1410 cm^{-1} and H_2O at 1606 cm^{-1}. The observation of two δ(HOD) vibrations indicates two types of adsorbed water. On evacuation, the preferential desorption of HOD from one site characterized by the 1450-cm^{-1} band was observed (Figure 7). When C_2D_2 is adsorbed onto a partially dehydrated sample of ZnNa–A the very rapid disappearance of the ν(OH) and $\delta(H_2O)$ vibrational bands of hydrogenous water and the appearance of ν(OD) and δ(HOD) vibrations is observed. This contrasts with the deuteration of OH groups in ZnNa–A using D_2O, where we have found exchange to be slow and incomplete, even at elevated temperatures. The deuteration of H_2O and OH on adsorption of C_2D_2 is clearly consistent with the formation of zinc acetylide and the release of D^+ into the zeolite framework, which is then able to rapidly exchange with the OH groups and zeolitic H_2O.

The importance of zinc acetylide formation in the hydration of C_2H_2 to ethanal is seen clearly in experiments on the adsorption of C_2H_2 by low-ion-exchanged ZnNa–A zeolite (sample 2). Here, three $\nu(C{\equiv}C)$ vibrations are observed at 1956, 1950, and 1942 cm^{-1} and no evidence for ethanal formation is detected, even after contact times of 21 h. The positions of the $\nu(C{\equiv}C)$ vibrations are in good agreement with those observed for $Na^+{-}C_2H_2$ complexes in Na–A zeolite,[10] where also no ethanal formation is detected over periods of prolonged contact. These findings indicated that in low-exchanged ZnNa–A C_2H_2 interacts with only the Na^+ cations, suggesting that the Zn^{2+} ions are located in sites inaccessible to C_2H_2 molecules, i.e., in sites within the sodalite cages. The formation of zinc acetylide is thus the important step in the hydration of C_2H_2 adsorbed on ZnNa–A zeolite.

4. Prolonged Ethyne Contact with Ag–A. The identification of ethanal as the product of C_2H_2 hydration on ZnNa–A zeolite prompted us to reexamine the adsorption of C_2H_2 by Ag–A zeolite[2] and in particular the effect of prolonged contact times. In the previous work a band observed at 1690 cm^{-1} was assigned to ν_4 of hydronium ions (H_3O^+). However, in view of the present study this mode is possibly due to ν(CO) of adsorbed ethanal. A sample of Ag–A from the same batch used previously was dehydrated under the same conditions (2 h at 673 K). When cooled to beam temperature bands at 3590–3300 cm^{-1} (ν(OH)) and 1648 cm^{-1} (δ(HOH)) showed that the sample had readsorbed significantly more water than was observed in the previous work. A weak band observed at 3610 cm^{-1} is due to structural hydroxyl groups. The data are summarized in Table III.

On adsorbing C_2H_2, ν(OH) and $\delta(H_2O)$ modes of the adsorbed water almost disappeared, and two new ν(OH) modes are observed at 3655 and 3584 cm^{-1}, showing the perturbation of these modes by the adsorbed C_2H_2. The $\nu(C{\equiv}C)$ modes of two π-bonded C_2H_2 species and of silver acetylide are observed at 1950, 1912, and 1816 cm^{-1}, respectively, and agree well with those published previously.[2] The ν(C-H) stretching vibrations of these species are observed at 3206 and 3171 cm^{-1}. These were previously not resolved.

The perturbation of the modes due to adsorbed water on C_2H_2 adsorption results from the release of H^+ on silver acetylide formation. In addition to the formation of new hydroxyl groups at 3655 and 3584 cm^{-1}, the loss of the features due to adsorbed water (1648 and 3590-3000 cm^{-1}) indicates a strong possibility that H_3O^+ is formed. A weak band observed ca. 2500 cm^{-1}, which was also seen in the previous study,[2] is assigned to the oxonium ion ($H_3O^+{\cdot}H_2O$). Corma et al.[18] have reported a band at 2510 cm^{-1} for this ion in type Y zeolites.

After C_2H_2 was in contact with Ag-A zeolite for 16 h, the ν(OH), ν(CH), and $\nu(C{\equiv}C)$ bands disappeared and two new bands were observed at 1719 and 1684 cm^{-1}. These are assigned to ν(CO) of ethanal hydrogen bonding to the framework OH groups and adsorbed on the Ag^+ cations, respectively.[17] The deformation and bending modes of the CH_3 and C-H groups are observed in the 1500-1300-cm^{-1} region. These assignments were confirmed by the adsorption on ethanal on Ag-A, which is described in detail elsewhere.[17]

After 16 h contact, difference spectra clearly indicate the reaction of both the π-bonded C_2H_2 and acetylide complexes. However, the present data do not provide sufficient evidence that both species are active in the formation of ethanal. It should be note that in our previous study a band observed at 1380 cm^{-1} remained unassigned. In view of our assignment of a band in the same region for ZnNa-A + C_2H_2 to a mode of the zinc acetylide complex, a similar assignment to silver acetylide seems reasonable.

Conclusions

The formation of both reacting and stable ethyne species has been observed when C_2H_2 (C_2D_2) is adsorbed onto ZnNa-A zeolite. A stable species, characterized by bands at 3238 (2403), 1955 (1731), and 763 cm^{-1}, has been identified as C_2H_2 π-bonding to the Na^+ cations through a side-on interaction. A second adsorbed species, characterized by bands at 3203 (2378), 1943 (1731), 1366, and 750 cm^{-1}, was found to react when left in contact with the zeolite. This complex has been identified as zinc acetylide (Zn—C≡C—H). The zinc acetylide was observed to react with zeolitic water to form ethanal, characterized by its adsorption bands at 1685, 1414, and 1355 cm^{-1}. In the case of C_2D_2, the release of D^+ into the zeolite on acetylide formation resulted in the very rapid exchange of zeolitic OH and H_2O, leading to a randomly deuterated product. The deuteration of the zeolitic water and OH groups was observed to be very much more efficient than that obtained by exchange with D_2O.

Ethyne adsorbed on low-exchanged ZnNa-A was found to interact with only the Na^+ cations. It was concluded that the Zn^{2+} cations were located in the sodalite cages where they are unable to form adsorption complexes with ethyne. No hydration of C_2H_2 to ethanal was observed.

The adsorption of ethyne on Ag-A zeolite has been reinvestigated. The reaction of the adsorbed ethyne with zeolitic water to form ethanal was observed. Although both the acetylide and π-bonded C_2H_2 were found to react, we envisage that the π-bonded species convert to the silver acetylide before hydration.

The hydration of ethyne to ethanal in the presence of zeolitic water has been found to occur via acetylide formation. No evidence for acetylide or ethanal formation was observed on low-exchanged ZnNa-A or Na-A zeolites, where only Na^+ ions interacted with the adsorbed ethyne. The formation of acetylide complexes thus seems to occur only in the presence of transition-metal cations and is the important step in the hydration of ethyne to ethanal.

Registry No. HC≡CH, 74-86-2; CH_3CHO, 75-07-0.

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Production and Fragmentation of Tantalum Carbide Cluster Ions

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The production and fragmentation of tantalum carbide cluster ions, $Ta_xC_y^+$ (x = 1-11, y = 1-26), have been studied by Fourier transform mass spectrometry. The cluster ions were generated by direct laser vaporization of a variety of metal- and carbon-containing samples, and the results were compared with previous studies that used Knudsen effusion mass spectrometry for the production of metal carbides. A study using isotopically labeled precursors was performed to determine the origin of the carbon species present in the $Ta_xC_y^+$ ions. All results are consistent with a mechanism involving gas-phase recombination reactions in the laser-generated plasma for the production of the $Ta_xC_y^+$ ions. The low-energy collision-induced dissociation reactions are dominated by loss of neutral C_3 and C_{10}. The TaC_y^+ ions can be considered to be an ionic metal center attached to a carbon cluster having either a linear or cyclic structure. Bridging metal-carbido ligands are suggested to be important for the larger $Ta_xC_y^+$ ions.

I. Introduction

Transition-metal carbides are characterized by their high melting points, great hardness, and metallic conductivity. These unique properties have led to numerous studies on the electronic structure and type of bonding present in the bulk carbides.[1-3] The majority of gas-phase metal carbide (M_xC_y) studies have used Knudsen effusion mass spectrometry to monitor the species in equilibrium in high-temperature ovens containing the metal of interest and graphite.[4-8] This technique has been used to study

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