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Spectroscopic Study of the Cyclotrimerization of Acetylene on NiY Zeolites. Influence of the Location of the Ni^{2+} Ions

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The cyclotrimerization of acetylene on NiY zeolites, containing 10, 14 and 19 Ni^{2+} ions/unit cell treated at 200 and 600°C, has been investigated by means of X-ray diffraction analysis, ir and EPR spectroscopies. It has been shown that this reaction does not alter the populations of Ni^{2+} ions in the different zeolitic cages. Comparison of the various samples has shown that their activity depends on the number of dehydrated or partly dehydrated Ni^{2+} ions inside the supercages. Cyclotrimerization of propyne can also occur. The effect of some ligands (NO, C_5H_5N, ND_3) on the cyclotrimerization of acetylene has also been examined. It has been established that the benzene formed does not remain bonded to the Ni^{2+} ions. Finally, the reduction of a small amount of Ni^{2+} ions into Ni^+ and Ni^0 species has been shown by EPR and one EPR signal was tentatively assigned to a $Ni(C_2H_2)_n^+$ species.

INTRODUCTION

Molecular sieves provide a choice material to study the nature of active sites in catalysis. Unlike in amorphous catalysts, atom positions may be determined by X-ray diffraction experiments. This is of interest especially when exchangeable cations are involved in a catalytic process. Then crystal structure analysis allows one to locate cations within the zeolite cages and thus may provide a good estimate of the number of cations accessible to reagents entering the porous framework. However previous studies performed in this laboratory (*1, 2*) have shown that cation displacements may occur upon reagent adsorption. Therefore the crystal structure of the zeolite must be determined not only before but also after the catalytic reaction in order to obtain a definite picture of the cations which may be involved.

Crystal structure of nickel Y zeolites containing 10, 14 and 19 Ni^{2+} ions/unit cell has recently been investigated and the location and therefore the accessibility of Ni^{2+} ions were determined (*3*).

In order to illustrate the interest of these data, the study of cyclotrimerization of acetylene known to be catalyzed by NiY zeolites (*4*) has been carried out. It has been verified that no significant change in cation distribution occurs during the reaction. Infrared and EPR spectroscopies have been used to determine the role of the location of the Ni^{2+} ions and of the dehydroxylation as well as to obtain a better understanding of the reaction mechanism.

EXPERIMENTAL METHODS

Materials. The starting material was a NaY zeolite supplied by Linde Co. Sodium ions were partly exchanged by nickel ions using an aqueous $Ni(NO_3)_2$ solution as described previously (*3*). The three samples obtained contained 10, 14 and 19 Ni^{2+} ions/unit cell (u.c.) and will be designated Ni-10, Ni-14 and Ni-19, respectively.

Acetone was removed from cylinder acetylene by allowing the gas to bubble through concentrated sulfuric acid. Then C_2H_2 was dried over a Linde 5 A molecular sieve and finally vacuum distilled over the sample. Other reagents were also purified and thoroughly dried.

Procedures. Infrared wafers (18 mm diameter) of ca. 30 mg of zeolite were compressed at a pressure of 1000 kg cm^{-2}. The quartz sample holder and cell were the same as in Ref. (*5*) with no joint or stopcock. For EPR and X-ray experiments the powder, activated in a quartz cell, was then transferred under vacuum into EPR tubes and X-ray capillaries.

For activation all samples were evacuated at room temperature, then heated at 200 or 600°C in oxygen for 5 to 10 hr and finally evacuated at the same temperature overnight in a greaseless vacuum line. They were then exposed at room temperature with acetylene under a 100 Torr pressure for 24 hr in the case of X-ray experiments and under various pressures for different times in the case of ir and EPR experiments.

All recordings were performed at room temperature (ir and X-rays) or at −196°C (EPR). A Perkin-Elmer model 125 ir spectrophotometer and Varian V 4502 and E 12 EPR spectrometers were used. The g values were determined using a dual cavity and DPPH sample as a reference ($g = 2.0036$). Some EPR recordings were performed at liquid helium temperature in a cold-finger Dewar adapted for the E 12 spectrometer. No EPR spectrum has been recorded for our initial NaY sample, which indicates that impurities such as Fe^{3+} or Mn^{2+} are not present within the limit of detection of the EPR spectrometer. When necessary, samples were irradiated in a ^{60}Co cell at −196°C for doses of about 5 Mrad. Crystal structures were determined from powder data using the X-ray techniques described elsewhere (*1*).

RESULTS

I. *X-Ray Study*

The distribution of scattering matter on cation sites found for 200 and 600°C-treated Ni-14 samples is almost the same before and after introduction of C_2H_2. Accordingly the electron density peaks on S_I, $S_{I'}$ (0.05), $S_{I'}$ (0.08), $S_{II'}$ (0.21) and S_{II} sites were assigned to Ni^{2+}, Na^+ ions and water molecules as in Ref. (*3*). No significant extra framework peak was observed which tends to indicate that C_2H_2 or the reaction products have no definite position inside the zeolite cages. Table 1 gives the cubic unit cell constants, the final R indexes and the nature, population and coordinates of the extra-framework localized species. Listings of observed and calculated structure factors and the complete pattern of atomic parameters corresponding to the structures discussed in this paper are available from the authors. It is interesting to note that acetylene molecules do not give rise to an important change in the Ni^{2+} ion population of the various cages (Table 2).

On the other hand, it may be noticed that the population N of the hexagonal prisms and the unit cell constant a of samples contacted with acetylene are not in accordance with the chart N vs a given in Ref. (*3*). For instance according to the chart, a should be equal to 24.49 Å for the 600°C-treated Ni-14 sample instead of the observed value of 24.44 Å. This decrease is not related to a displacement of Ni^{2+} ions towards the hexagonal prisms discussed elsewhere (*29*).

II. *Infrared Study*

Bands Due to C_2H_2

After admission of ~5 Torr of C_2H_2 to all NiY samples, two CH stretching bands (ν_3) appear around 3215 and 3240 cm^{-1}. In the spectrum of the 600°C-treated Ni-19 sample, these bands are difficult to observe since the formation of benzene takes place rapidly, as indicated later.

If the quantity of C_2H_2 admitted is greater (~20 Torr), the 3215 cm^{-1} band

TABLE 1
DISTRIBUTION OF EXTRA-FRAMEWORK SPECIES[a]

Sample	Final R index	Unit cell constant (Å) (±0.01)	S_I	$S_{I'}$	$S_{I'}$	$S_{II'}$	$S_{II'}$	S_{II}
200°C-treated Ni-14 + C_2H_2	0.082	24.59	3.3 (2) Ni 0.0	3.8 (3) Ni 0.057 (1)	3.1 (3) Ni 0.083 (1)	13.4 (1.2) Ow 0.165 (1)	3.4 (4) Ni 0.213 (2)	18.6 (1.7) Na 0.236 (1)
600°C-treated Ni-14 + C_2H_2	0.089	24.44	10.4 (3) Ni 0.0	1.3 (4) Ni 0.058 (4)				26 (1.7) Na 0.238 (1)

[a] The data tabulated consist of the number of species per unit cell, assignment of species type and its $x = y = z$ coordinates. Estimated standard errors are indicated in parentheses. Ow: means oxygen atom of water molecule or hydroxyl group.

is less visible, whereas the 3240 cm^{-1} band is enhanced. For higher pressures of C_2H_2 (~100 Torr), because of the ir cell used, it is difficult to distinguish the spectrum due to adsorbed C_2H_2 from the overlapping spectrum due to gaseous C_2H_2. Nevertheless, the relative intensities of the observed bands allow one to infer that adsorbed C_2H_2 has an intense band at 3250 cm^{-1} and perhaps a weaker one around 3300 cm^{-1}.

Under similar conditions, bands at approximately the same frequencies also occur in the case of a NaY zeolite.

In gaseous C_2H_2, the stretching C≡C vibration (ν_2) is infrared inactive and appears at 1974 cm^{-1} in the Raman spectrum (*6*). In the case of C_2H_2 adsorbed on a NiY sample, a very weak band occurs near 1950–1955 cm^{-1}. For pressures of ~100 Torr, another very weak band is observed at 1975 cm^{-1}.

The ν_2 and ν_3 bands of adsorbed C_2H_2 are removed by evacuation at room temperature.

The information which may be inferred from the C_2H_2 bands is presented in the Discussion.

Formation of C_6H_6

When exposing a 600°C-treated Ni-19 sample to C_2H_2 ($p \sim 5$ Torr) 3 bands occur in the 3100–3000 cm^{-1} region (Fig. 1b) and 4 bands in the 2000–1400 cm^{-1} region (Fig. 2b). Further exposure leads to an increased intensity in these bands (Figs. 1c and 2c) and to the complete disappearance of the bands due to C_2H_2 (Fig. 1c). The new bands observed have frequencies close to those found by several authors (*7–9*) in the case of benzene adsorbed on various cation-exchanged zeolites. With respect to liquid benzene, shifts in frequencies and changes in relative intensities are found. In particular, the ratio of the intensity of the ring vibration ν_{19} to the intensity of the CH stretching vibration is enhanced. This suggests that the benzene molecules are bonded to the zeolite via their π electrons in a direction perpendicular to the plane of their ring (*8*).

On the same 600°C-treated Ni-19 sample, it is possible to introduce new amounts of C_2H_2 and to observe an increase in the bands assigned to C_6H_6 whereas the bands of C_2H_2 disappear. The process can be repeated up to a limit which probably corresponds to the filling of the zeolitic cavities with C_6H_6. It is interesting to mention that the ratio of the intensity of the ν_{19} vibration band to the intensity of the CH stretching bands decreases with increasing amount of C_6H_6 formed, suggesting a change in the mode of bonding of C_6H_6 to the zeolite.

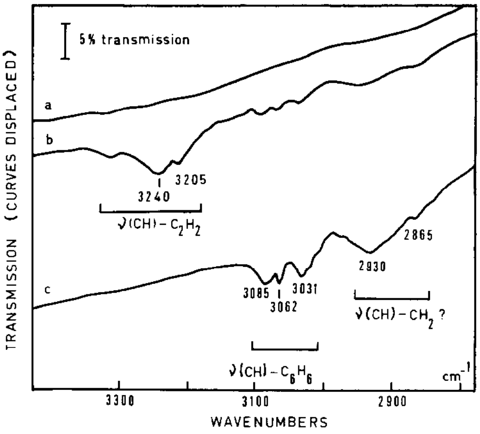

FIG. 1. Infrared spectra (3400–2800 cm^{-1}) of a 600°C-treated Ni-19 sample: (a) before introduction of C_2H_2, (b) 20 min after introduction of ≃5 Torr of C_2H_2, (c) 3 hr after the C_2H_2 introduction.

The benzene thus formed can be completely removed by evacuation at 100°C or by heating the zeolite at 100°C and trapping the product evolved.

The formation of benzene has been studied on the NiY zeolites for two temperatures of pretreatment. The results are listed in the last column of Table 2.

Comparison between samples treated at 600°C shows that: (i) the cyclotrimerization is rapid with 5 Torr of C_2H_2 on the Ni-19; (ii) the pressure of C_2H_2 must reach ~100 Torr to obtain a fast trimerization on the Ni-14; (iii) only traces of C_6H_6 are formed on the Ni-10 after 24 hr exposure, whatever the pressure. Thus cyclotrimerization does not take place for a too low Ni content and then its rate increases with increasing Ni content.

For low pressures of C_2H_2 the reaction

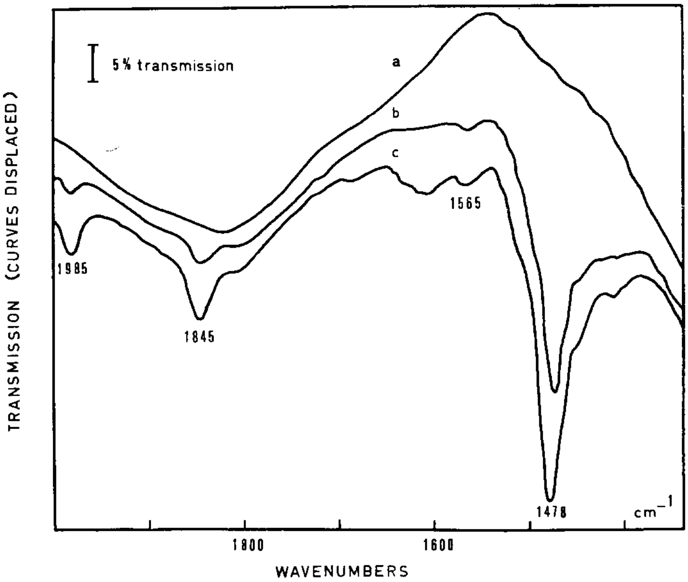

FIG. 2. Infrared spectra (2000–1400 cm^{-1}) of a 600°C-treated Ni-19 sample: (a) before introduction of C_2H_2, (b) 20 min after introduction of $\simeq$5 Torr of C_2H_2, (c) 3 hr after the C_2H_2 introduction.

is slow on the 200°C-treated Ni-19 sample and yields only traces of C_6H_6 on the 200°C-treated Ni-14 sample. However, after 20 min it becomes rapid on both samples for pressures of ~100 Torr of C_2H_2. On the Ni-10 sample treated at the same temperature only traces of C_6H_6 are obtained after 24 hr. Thus the degree of dehydration of the samples affects the rate of the cyclotrimerization.

TABLE 2

Ni^{2+} ION LOCATION AND C_6H_6 FORMATION

Samples	Ni^{2+} ions/u.c. in the various cages Hexagonal prisms	 Sodalite cages	 Super-cages[a]	C_6H_6 formation according to pressure of C_2H_2
600°C-treated Ni-10[b]	8.8	1.7	~0	Traces for $p_{C_2H_2} \simeq 50$ Torr after 24 hr
600°C-treated Ni-14[b]	11.7	1.1	1.2	Small amount for $p_{C_2H_2} \simeq 5$ Torr; fast reaction for $p_{C_2H_2} \simeq 100$ Torr
600°C-treated Ni-14[c]	10.4	1.3	2.3	
600°C-treated Ni-19[b]	11.3	1.9	5.8	Fast reaction for $p_{C_2H_2} \simeq 5$ Torr
200°C-treated Ni-10[b]	4.4	5.7	~0	Traces for $p_{C_2H_2} \simeq 50$ Torr after 24 hr
200°C-treated Ni-14[b]	4.1	8.6	1.3	Traces for $p_{C_2H_2} \simeq 5$ Torr after 15 h; fast reaction for $p_{C_2H_2} \simeq 100$ Torr after 20 min delay
200°C-treated Ni-14[c]	3.3	10.3	0.4	
200°C-treated Ni-19[b]	3.6	12.5	2.9	Very slow reaction for $p_{C_2H_2} \simeq 5$ Torr; fast reaction for $p_{C_2H_2} \simeq 100$ Torr after 20 min delay

[a] These numbers were obtained by subtracting the number of Ni^{2+} ions located in the hexagonal prisms and the sodalite cages from the total number of Ni^{2+} ions.

[b] Ni^{2+} ion location determined before introduction of C_2H_2 (*3*).

[c] Ni^{2+} ion location determined after introduction of C_2H_2.

The influence of the preadsorption of some molecules on the cyclotrimerization of C_2H_2 has been investigated. NO chemisorbed (main band at 1898 cm^{-1}) at room temperature on a 600°C-treated Ni-19 sample precludes the formation of C_6H_6. ND_3, remaining adsorbed after evacuation at 100°C, gives bands in the 2550–2300 cm^{-1} region (the corresponding bands of NH_3 would have restricted the observation of the bands of C_2H_2 and C_6H_6). Five minutes after the introduction of 80 Torr of C_2H_2, benzene is formed. Pyridine remaining adsorbed at 150°C has the same effect as NO.

The bands of adsorbed benzene are not the only bands occurring in the spectrum as a result of the disappearance of C_2H_2. Two bands appear at ca. 2930 and 2865 cm^{-1} and grow gradually (Fig. 1). They are tentatively assigned to CH_2 groups although their relative intensities differ from those observed in the case of liquid hydrocarbons. The CH_2 scissor vibration is expected around 1470 cm^{-1}. This band of weak intensity may be overlapped by the strong band of benzene at 1478 cm^{-1}. Simultaneously, the transmission of the zeolite diminishes progressively and the color of the sample darkens. This darkening may be due to the reduction of some of the Ni^{2+} ions to Ni^0 species (see EPR results) and/or to the formation of carbonaceous residues coming, like the CH_2 groups, from the disproportionation of C_2H_2.

Cyclotrimerization of Propyne

In order to elucidate whether the Ni exchanged zeolites are capable of cyclotrimerizing an alkyne other than C_2H_2, the adsorption of propyne was performed. At the same time, this study was of interest to determine the effect of the Ni^{2+} ions on the $\nu(C{\equiv}C)$ stretching vibration of an unsymmetrical alkyne. Propyne was chosen because it is the smallest unsymmetrical alkyne. Fig. 3 shows that the frequency of the $\nu(C{\equiv}C)$ band observed in the case of the 600°-treated Ni-19 sample does not differ from that obtained with a NaY sample pretreated at the same temperature. But in the same experimental conditions the optical density of the C≡C stretching band, 20 min after the admission of C_3H_4 (pressure $\simeq$ 5 Torr), is much lower in the case of the Ni exchanged zeolite and the band gradually decreases on further contacting with C_3H_4 (Fig. 3). Simultaneously bands appear in the 1700–1350 cm^{-1} region (Table 3) and, in particular, the band around 1600 cm^{-1} is characteristic of the formation of aromatic compounds.

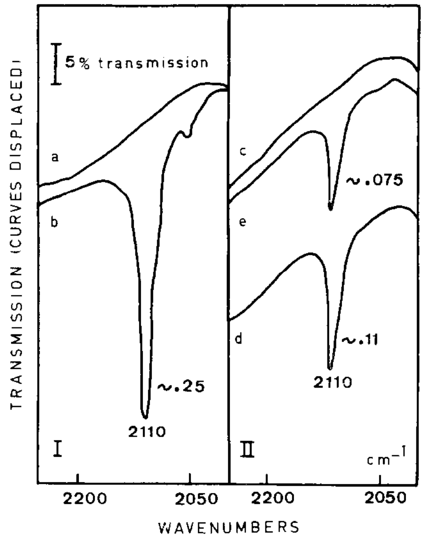

FIG. 3. Optical densities of the (C≡C) stretching band of propyne adsorbed on the 600°C-treated NaY (I) or NiY (II) samples: (a) and (c) before introduction of C_3H_4; (b) at various times after introduction of $\simeq$5 Torr of C_3H_4; (d) and (e) 20 min and 3 hr, respectively, after introduction of $\simeq$5 Torr of C_3H_4.

The products of the cyclotrimerization of propyne can be the 3 trimethylbenzenes. According to Whitesides and Ehmann (*10*), the distribution of the 3 isomers is (1,2,4) > (1,3,5) > (1,2,3) $\geqslant$ 0, whatever the mechanism. Comparison of the frequencies and intensities of the ir bands of the 3 isomers (Table 3) with those observed when contacting propyne with NiY zeolites tends to show that cyclotrimerization of propyne does take place. As expected, the main product seems to be the (1,2,4) isomer. The weak intensity of the 1495 cm^{-1} band may be due to the presence of the other isomers (one or two) or/and related to differences between adsorbed and

TABLE 3

Main Vibration Frequencies (in the 1650–1350 cm^{-1}Region) for Trimethylbenzenes and the Compounds Resulting from the Contact of Propyne with the Ni-19 Sample[a]

Propyne on Ni-19 after evacuation at 25°C	1598 s	1495 sh, m	1450 vs	1382 s
Liquid trimethylbenzenes (1, 2, 4)	1619 s	1506 vs	1452 vs	1384 s
(1, 3, 5)	1609 vs		1472 s, 1442 m	1376 s
(1, 2, 3)	1588 s		1476 vs, 1444 s	1386 s, 1379 s

[a] Intensities of the bands: m, medium; s, strong; vs, very strong; sh, shoulder.

liquid states. Weak bands are also found in the CH stretching region but are mainly due to CH_3 groups and are too weak to be useful to specify the nature of the formed compounds. On the other hand, it is impossible to check the nature of these compounds by desorbing them, since they crack between 250 and 300°C before desorbing, probably because of their size, which does not allow easy removal from the zeolitic cavities.

III. *EPR Study*

None of the 200 and 600°C treated NiY samples were found to give an EPR spectrum at liquid helium or nitrogen temperatures but introduction of C_2H_2 produces EPR signals on the latter samples. In the case of samples exposed to 5 Torr of C_2H_2 these signals occur rapidly for Ni-19 samples, whereas several hours are needed for Ni-10 and Ni-14. With higher C_2H_2 pressures (e.g., 100 Torr) they occur rapidly for all samples. Moreover, it has been observed that aliphatic hydrocarbons such as ethane and isooctane do not give rise to EPR spectra even in the case of 600°C-treated samples in contrast to unsaturated hydrocarbons such as ethene, butene, acetylene and propyne.

A typical EPR spectrum obtained after introduction of acetylene on a 600°C-treated NiY sample is shown in Fig. 4. It is composed of four different signals labeled I to IV and listed in Table 4. The number of paramagnetic species corresponding to signals II to IV is small ($\simeq 10^{18}$ spins/g) for all samples. The intensity of signal I depends on nickel content and time of contact.

Signal I

Signal I is not detectable for low C_2H_2 pressures and short exposure times, presumably because of its very broad line width. Its intensity slowly increases with

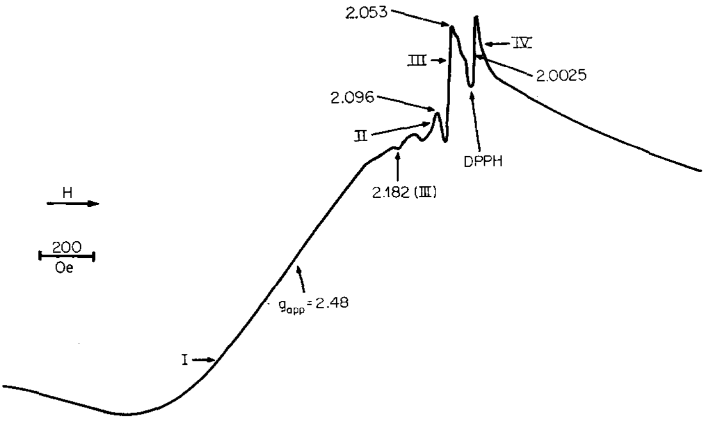

Fig. 4. EPR spectrum of a 600°C-treated Ni-19 sample after introduction of 100 Torr of C_2H_2 for several hours of contact and subsequent outgassing at room temperature. The spectrum is recorded at −196°C.

TABLE 4
EPR PARAMETERS OF SIGNALS OBSERVED ON 600°C-TREATED NiY SAMPLES AFTER INTRODUCTION OF C_2H_2

Signal	g_{app}	$g_{\parallel}$	$g_{\perp}$	ΔH_{pp} (Oe)	Comments	Assignment
I	2.5	—	—	900/1400	Broad and unresolved	Ni^0
II	—	2.2–2.4	2.096	—	Axially symmetrical	Ni^+
III	—	~2.18	2.053	—	Ill resolved (5 or 7 hyperfine lines with a 12 Oe splitting)	$Ni(C_2H_2)_n{}^+$ $n = 2$ or 3
IV	2.002	—	—	14	Unresolved	Carbon

time and markedly with Ni content. Nevertheless this intensity remains very small, approximately 10 or 100 times weaker than that obtained when the sample is reduced by molecular hydrogen at 340 or 450°C, respectively. This signal is only observable after action of C_2H_2 and is characteristic of ferromagnetic resonance due to Ni^0 species which stem from slow reduction of few Ni^{2+} ions by C_2H_2. Ni^0 species are not detected by X-ray analysis, because either their number is too low or the particles formed are too small.

Signal II

The formation of Signal II greatly depends on nickel content and acetylene pressure. Without C_2H_2 it has also been observed for all 200 and 600°C samples after γ irradiation at −196°C. When the samples are reduced by molecular hydrogen at 340°C, it is found superimposed on signal I, but it disappears after H_2 reduction at 450°C. Consequently, the species responsible for this signal are difficult to reduce.

The EPR parameters (Table 4) are quite similar to those reported by Rabo *et al.* (*11*) for Ni^+ ions (Fig. 5). Ni^+ ions are isoelectronic with Cu^{2+} ($3d^9$) studied in detail by Bleaney, Bowers and Pryce (*12*). For Cu^{2+} ions in a tetragonally distorted octahedral ligand field $g_{\parallel} \gg g_{\perp} > g_e$ (*12*), whereas in a tetrahedral coordination

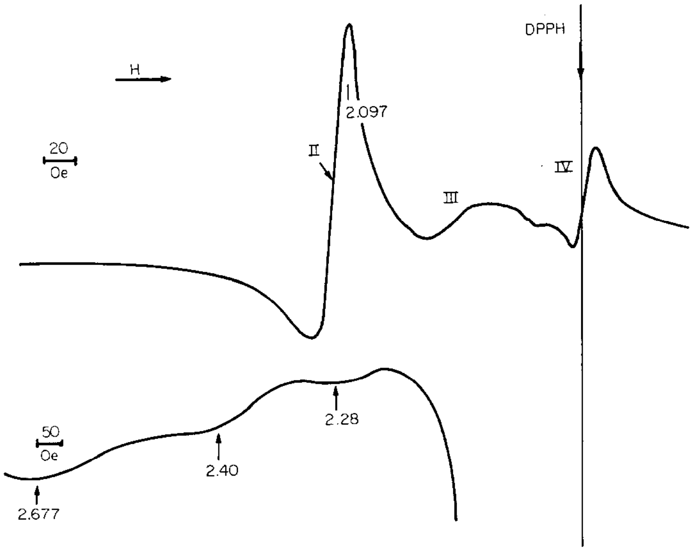

FIG. 5. EPR spectrum of a 600°C-treated Ni-14 sample after introduction of 100 Torr of C_2H_2 for 15 min. The spectrum is recorded at −196°C.

$g_e \simeq g_\parallel \ll g_\perp$ (*13*). Consequently, one may suggest that signal II corresponds to slightly distorted octahedral Ni^+ ions. It seems reasonable to locate these Ni^+ ions in the S_I site as suggested in Ref. (*11*) since their reduction by hydrogen is difficult.

Signal III

As mentioned above signal III has only been observed when unsaturated hydrocarbons are introduced over the samples. EPR parameters $g_\parallel \gg g_\perp > g_e$ may indicate that it is due to a Ni^+ ion in a distorted octahedral ligand field. It has been shown that when ammonia or pyridine are contacted with $Cu^{2+}Y$ zeolite, Cu^{2+} ions coordinate with four ligand molecules and a shift of the g values towards g_e occurs (*14*, *15*). Similar shifts are observed between the g values of signals II and III. This seems to favor the assignment of signal III to a complex between Ni^+ ions and C_2H_2 molecules. For some experiments, an ill-resolved hyperfine structure of 5 or 7 lines with a ca. 12 Oe splitting does appear on the perpendicular component of signal III as shown in Fig. 6, the resolution being strongly dependent on acetylene pressure. In this system only protons have a nonzero nuclear spin (the ^{61}Ni isotope with $I = 3/2$ is only 1.25% abundant in nature) and 5 or 7 hyperfine lines correspond, respectively, to 4 or 6 equally coupled protons. Consequently, we tentatively suggest that signal III may be attributed to a $Ni(C_2H_2)_n^+$ complex with $n = 2$ or 3. The hyperfine splitting is consistent with this complex, since, for a $Ni(C_6H_6)^+$ complex, one would have expected a much smaller splitting, at least inferior to the corresponding 4.4 Oe value of the $C_6H_6^+$ cation (*16*).

Signal IV

Signal IV can be assigned to carbon impurities which stem from the cracking or dismutation of acetylene.

Signals Observed After γ Irradiation

If cyclotrimerization of C_2H_2 takes place, benzene is formed. However, benzene molecules which have a high ionization potential (~9.3 eV), are not ionizable into paramagnetic radicals by the catalyst (*17*). Their ionization may be obtained by irradiation of the NiY samples at −196°C. Figure 7 represents a well-resolved benzene cation spectrum observed on a 600°C-treated Ni-14 sample after outgassing C_2H_2 at room temperature. The spectrum is similar to that obtained by irradiation at −196°C of a small amount of benzene adsorbed on a HZ zeolite (*16*). The stick diagram, given in Fig. 7, corresponds to seven hyperfine lines with a small anisotropy: $g_\parallel = 2.0022$, $g_\perp = 2.0024$, $C_\parallel = 4.0$

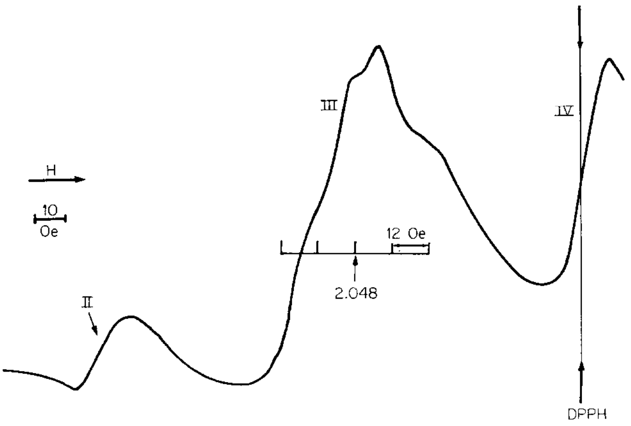

FIG. 6. EPR spectrum of a 600°C-treated Ni-19 sample after introduction of about 5 Torr of C_2H_2 for several hours. The spectrum is recorded at −196°C.

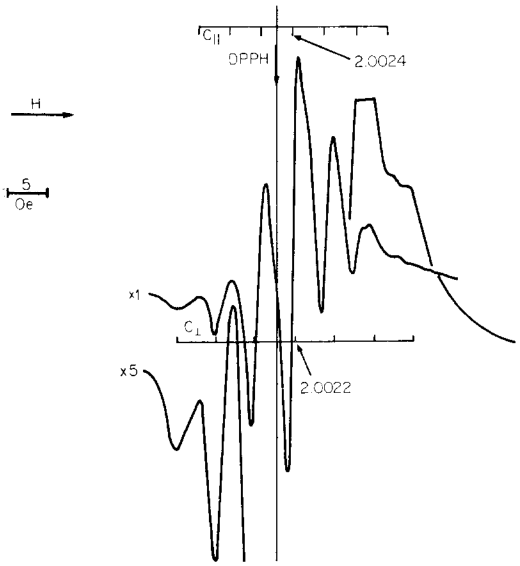

FIG. 7. Benzene cation spectrum compared to the theoretical stick diagram. The Ni-14 600°C-treated sample has been contacted with 100 Torr of C_2H_2 for 15 min, then outgassed at room temperature for several hours, γ irradiated and recorded at liquid nitrogen temperature.

Oe, $C_{\perp} = 5.0$ Oe, $b = 0.3$ Oe and $a^H = 4.7$ Oe. It may be attributed to the benzene cation since the theoretical value is $a^H = 26.6/6 = 4.4$ Oe. The EPR parameters show that rapid rotation of the benzene molecule takes place about the molecular sixfold axis, which indicates that the molecules are weakly adsorbed on the zeolite via their π electrons and no complex of the type $Ni(C_6H_6)^+$ is formed.

When acetylene is not outgassed before irradiation the EPR spectrum is much more complex. It is composed of the former heptet, of a 13 hyperfine line signal with $a^H = 2.2$ Oe and a complex signal with large hyperfine splittings. The 13 hf line spectrum is also observed when an excess of benzene is adsorbed on NiY and NaY zeolite samples irradiated at −196°C. The hf splitting being equal to half the theoretical one for benzene cation, the 13 hf line spectrum may correspond to the radical cation dimer of benzene, the unpaired electron being equally shared between two benzene rings, presumably in a sandwich-like configuration (*17*, *18*). Such a spectrum has mainly been observed on the Ni-19 samples which tends to prove that more benzene is formed on that sample compared to the two other ones, in good agreement with ir data.

The spectrum with large hyperfine splittings (~15 Oe) has not been identified because of its poor resolution and to the overlapping of benzene signals. However, the large value of the hf splittings characterizes nonaromatic molecules.

If irradiation is performed on the 200°C-treated samples which are contacted with C_2H_2, signals I to IV and benzene cation are observed. This indicates that cyclotrimerization occurs as observed by ir, but signals I to IV appearing only after irradiation are probably due to the irradiation which may dehydrate the samples (*19*).

Signals Obtained with Propyne

If the samples are contacted with propyne, composite signals are obtained. The spectra are complicated by the small aromatic proton splittings of the order of the line width and cations coming from trimethylbenzenes cannot be identified with certainty. However, signals I to IV occur with similar intensities in the same conditions as with C_2H_2, which indicates that the reduction of the Ni^{2+} ions and their complexing are not limited to acetylene but can be extended to other alkynes capable of reaching the Ni^{2+} ions.

DISCUSSION

Influence of the Location of Ni^{2+} Ions Upon the Cyclotrimerization

Very slight changes occur in the Ni^{2+} ion distribution inside the different cages after 24 hr of contact with acetylene and benzene formed by cyclotrimerization (Table 2).

Only the Ni^{2+} ions occupying the supercages need to be taken into account to explain the results concerning the cyclotrimerization because (i) C_2H_2 molecules cannot reach and complex the Ni^{2+} ions inside the hexagonal prisms, and (ii) the Ni^{2+} population in the sodalite cages is roughly constant for the three 600°C-treated samples, whereas the amount of C_6H_6 formed varies from traces (Ni-10) up to the filling of the supercages (Ni-14 and Ni-19). Infrared results show that the benzene formed can be completely removed from the zeolite. Consequently, the Ni^{2+} ions in the sodalite cages seem to be inactive to produce significant amounts of benzene, since C_6H_6 molecules cannot escape through the 2.3 Å sodalite cage aperture.

The different rates of cyclotrimerization observed with samples treated at 600°C and exposed to low acetylene pressure are quite consistent with the above statements. These rates estimated from ir results and corroborated by EPR data follow the sequence Ni-19 > Ni-14 > Ni-10 $\sim$ 0 as do the number of Ni^{2+} ions in the supercages derived from the X-ray investigation. For higher C_2H_2 gas pressures they are enhanced, possibly because the collision probability of C_2H_2 molecules with Ni^{2+} ions is increased, but the Ni-10 sample remains almost inactive.

Since the only active sites for the cyclotrimerization of acetylene are the Ni^{2+} ions occupying the supercages, a completely dehydrated NiY zeolite becomes active only when the exchange level is raised above $\sim$12 Ni^{2+}/u.c., namely the number of Ni^{2+} ions accommodated in hexagonal prisms and sodalite cages.

Influence of Residual Water Molecules and Other Ligands Upon the Cyclotrimerization

The ir experiments have shown that (i) the Ni-10 sample is almost inactive whatever the temperature of treatment, and (ii) the 200°C-treated Ni-14 and Ni-19 samples are far less active than those treated at 600°C. Thus, a longer time and a higher pressure of C_2H_2 are needed to observe the formation of a given amount of benzene and the reaction requires about 20 min before accelerating.

These observations indicate that the H_2O molecules (or OH groups) which remain in the zeolite after a 200°C-treatment hinder the catalyst activity. Unfortunately, this cannot be easily interpreted because the precise hydration state of Ni^{2+} ions occupying the supercages is unknown. However, the two following extreme conditions can be discarded: (i) the Ni^{2+} ions are entirely free from coordinated water, since, in this case, the reaction should take place immediately and for low C_2H_2 pressure, and (ii) all Ni^{2+} ions are involved in hexaquo complexes, since, in this case, the zeolite should be inactive whatever the time of the contact and C_2H_2 pressure, because the strong crystal field of water prevents acetylene from displacing the H_2O ligands so that no nickel–acetylene complex is formed.

Therefore it may be expected that a small part of the Ni^{2+} ions have some vacant orbitals to ensure the cyclotrimerization. Alternatively, the Ni^{2+} ions may be bonded to water molecules and to framework oxygens with the possibility of the C_2H_2 molecules breaking the latter bonds to complex Ni^{2+} ions.

In order to study the influence of the ligand strength, adsorption of NO or C_5H_5N has been carried out on 600°C-treated Ni-19 samples before C_2H_2 introduction. These molecules prevent the cyclotrimerization because they form strong bonds with Ni^{2+} ions in the supercages and probably complex them entirely. On the other hand such a behavior constitutes an indirect evidence of the role played by Ni^{2+} ions in the reaction. On the contrary, ND_3 remaining adsorbed after evacuation at 100°C does not preclude the cyclotrimerization. It has been shown (*2*) that NH_3 molecules induce an important migration of Ni^{2+} ions from hexagonal prisms to sodalite cages and supercages. Subsequent evacuation at 100°C removes some of the NH_3 ligands from part of the Ni^{2+} ions so that this partly deammoniated sample may be compared to the corresponding partly dehydrated sample. However, this ammoniated sample contains more Ni^{2+} ions in the supercages, consequently it is capable of forming benzene more rapidly.

Complexes Between Nickel Ions and Acetylene Molecules

It has been shown that C_2H_2 molecules give rise to a paramagnetic species (signal III) assigned to a complex between one

Ni^+ ion and 2 or 3 C_2H_2 molecules, which implies the reduction of Ni^{2+}. One may then tentatively postulate that this complex is involved in the catalytic process mechanism. Nevertheless, this complex seems too stable to liberate C_6H_6, since it does not disappear at room temperature after a long period of contact under a 5 Torr C_2H_2 pressure and subsequent outgassing. Moreover, its concentration is very small and remains roughly constant for the three samples. Finally, Ni^+ is isoelectronic with Cu^{2+} which does not cyclotrimerize C_2H_2 (*4*). So, the $Ni\ (C_2H_2)_n^+$ complex probably corresponds to a side reaction. On the other hand, paramagnetic complexes between Ni^{2+} ($S = 1$) and C_2H_2 have not been observed by EPR because either they do not exist or, like Ni^{2+} ions, they are not detectable. Information given by ir experiments on the possible formation of these complexes is discussed below.

Table 5 indicates that the asymmetric stretching band CH of C_2H_2 has been observed in the 3300–3086 cm^{-1} region and that adsorbed acetylene absorbs in the 3300–3205 cm^{-1} region. The bands of C_2H_2 adsorbed on the NiY zeolites are included in this latter range, but do not seem peculiar to the NiY zeolites, since bands at similar frequencies are observed in the case of NaY zeolites. In the C≡C stretching region the bands found have very weak intensities.

If it is assumed that the C_2H_2 molecules bonded to the Ni^{2+} ions have characteristic frequencies, these molecules are not detected by means of ir spectroscopy, perhaps because of their very low amount at a given time. Alternatively, it may be assumed, considering Table 5, that if the complex is not stable, the C_2H_2 molecules do not have characteristic frequencies and that, consequently, their ir bands are blurred in the absorption due to the molecules of C_2H_2 adsorbed on other sites.

More information on the nature of the bond between an alkyne and the Ni^{2+} ions was expected from the shift of the stretching frequency $\nu(C{\equiv}C)$ of the propyne adsorbed. But the observed shift is only ~30 cm^{-1} and does not differ from that found in the case of a NaY sample.

In conclusion we have not been able to observe distinct ir bands or EPR signals directly proving the existence of complexes between Ni^{2+} ions and C_2H_2 or C_3H_4 molecules.

Mode of Adsorption of Benzene

From the EPR results it may be concluded that complexes like $Ni(C_6H_6)^+$ are not formed and that benzene molecules are freely rotating about their sixfold axis. Thus, these molecules are only weakly adsorbed on the zeolite, via their π electrons, and do not poison the cyclotrimerization. It has also been shown that in the presence of an excess of benzene, the molecules are bonded in pairs in a sandwich-like configuration.

Some support to the existence of two types of adsorbed benzene molecules is given by the ir results. In agreement with other authors (*7–9*), the differences observed between the spectra of C_6H_6 in liquid and adsorbed states are explained by the interaction between the π orbital of the aromatic compound and the zeolite in a direction perpendicular to the plane of the ring. Moreover, the decrease in the ratio of the intensity of the ν_{19} vibration band to

TABLE 5

WAVENUMBERS (cm^{-1}) OF C_2H_2 IN VARIOUS STATES[a]

ν_1(C—H *sym*)	3374 g, R (*6*); 3290 a, $CuCl_2/SiO_2$ (*26*); 3116 $CH{\equiv}CHCo_2\ (CO)_6$ (*28*)
ν_3(C—H *asym*)	3300 a, Al_2O_3 (*20, 21*); 3289 g (*6*); 3283–3134 in various solvents (*22, 27*); 3263 s (*20*); 3265-50 a, SiO_2, porous glass (*20, 23*); 3225 C_2Na_2 (*24*); 3220 a, Al_2O_3 (*20, 21*); 3228-10 a, zeolites A and X (*25*); 3228-05 a, $M^{II}Cl_2/SiO_2$ (*26*); 3086 $CH{\equiv}CHCo_2\ (CO)_6$ (*28*)
ν_2(C≡C)	2007 a, Al_2O_3 (*20, 21*); 1974 g, R (*6*); 1950 a, Al_2O_3 (*20, 21*); 1867 C_2Na_2 (*24*); 1818 a, $CuCl_2/SiO_2$ (*26*); 1402-5 $CH{\equiv}CHCo_2\ (CO)_6$ (*28*)

[a] a = adsorbed, g = gas, l = liquid, R = Raman, s = solid.

the intensity of the CH stretching bands when the amount of C_6H_6 formed increases (Figs. 1, 2), tends to indicate a change in the environment of the benzene molecules, provided that the increase in the degree of filling of the cavities does not imply a marked alteration in the extinction coefficients. Therefore the spectrum of C_6H_6 tends to resemble that of the liquid and may account for the sandwich-like species suggested by the EPR results.

Other Species

Cyclotrimerization is not the only reaction which occurs. Other species (Ni^0, Ni^+, $-CH_2$), found in small amount, indicate that dismutation of C_2H_2 and reduction of Ni^{2+} ions take place. We have suggested that Ni^+ ions, formed by reduction of Ni^{2+} ions by C_2H_2 at room temperature but difficult to reduce by molecular hydrogen into Ni^0 species, are located in S_I sites. Such ions are chemically unstable, but they are probably stabilized by the octahedral coordination within the zeolitic framework. The amounts of Ni^0 and $-CH_2$ species increase with time of contact and nickel content. These species remain in the zeolite after desorption of the benzene.

CONCLUSION

This work on the acetylene cyclotrimerization represents an interesting illustration of the role of the location and environment of the cations in zeolites.

Using three physical techniques, the experimental conditions required to obtain an active NiY zeolite for this reaction have been determined and their choice has been explained in terms of the accessibility of the Ni^{2+} ions. It follows that the reaction occurs if the NiY zeolite fulfills at least two requirements: Ni^{2+} ions must be available in the supercages, and they must be dehydrated (or partly dehydrated). Then the rate of the reaction depends upon the number of these accessible Ni^{2+} ions. Since the dehydration produces a migration of Ni^{2+} ions up to a maximum of 12 towards the hexagonal prisms, a zeolite must contain additional Ni^{2+} ions in order to be active for the reaction.

It has been shown that the benzene obtained does not form a complex with the Ni^{2+} ions and is weakly adsorbed on the framework. Therefore it does not poison the reaction and can be easily extracted. However, present data are not sufficient to suggest a mechanism for the reaction since no active intermediate species has been detected.

Finally, it may be suggested that the acetylene cyclotrimerization may be used as a probe to estimate the amount of cations occupying the supercages of a given dehydrated zeolite provided these cations are catalytically active.

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