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Adsorption of Pyrrole on Fe(II)Y, Fe(III)Y, Cu(I)Y, and Cu(II)Y Zeolites

Pyrrole-type compounds are widely found in natural crude oil and are suspected poisons of refining catalysts such as Y zeolite (*1*). Transition metal impurities are present in zeolite and its binder. Metal concentration on the catalyst often increases during the refining process since these impurities are also present in the crude. Understanding the adsorption behavior of pyrrole on transition metal exchanged zeolites can thus provide insights into the problem of catalyst deactivation. In addition, since pyrrole-type compounds also exist in shale oil and are believed to be actively involved in the formation of gum during storage (*2*), this study may also offer a means to remove these compounds from fuel and provide a solution to this fuel instability problem.

Scokart and Rouxhet (*3*) studied the IR spectrum of adsorbed pyrrole on NaY zeolite and found that low amounts of pyrrole adsorbed onto the zeolite through NH interacting with weak basic sites on the zeolite framework. No work has been reported in the literature concerning the adsorption of pyrrole on transition metal cation exchanged Y zeolite. Pyrrole has been oxidatively polymerized by electrochemical means to form electrically conducting polypyrrole (*4*). It is believed that this polypyrrole consists of mostly α,α'-linkages and retains the unsaturated pyrrole ring moity as its repeating unit. Pyrrole can also be polymerized by ferric salts (*5*). The polymer synthesized chemically in an alcohol solution of pyrrole in the presence of sulfuric acid results in a more hydrogen-rich compound (*6*), but when pyrrole was treated with concentrated acid, a partially saturated trimer was isolated (*7*).

In this paper we report the results obtained from the adsorption of pyrrole on Fe- and Cu-exchanged Y zeolites. The study is aimed at exploring the roles the transition metal ions play in the adsorption and reaction of pyrrole on zeolites. Both the higher oxidation state ions Fe(III) and Cu(II) and the lower oxidation state ions Fe(II) and Cu(I) were examined. *In situ* IR was the major tool used for monitoring the surface reactions, and other analytical methods were also used to characterize the surface and the products.

NaY zeolite powder (Union Carbide, surface area 895 m^2/g) was purified by washing with NaCl (2 *M*). Fe(II)NaY zeolite was prepared by stirring the purified NaY with $FeSO_4$ solution under nitrogen atmosphere. The Fe-exchanged NaY was 72% exchanged (determined by AA). The CuNaY sample was prepared similarly but with a solution of $Cu(NO_3)_2$. The final pH of the ion exchange solution was equal to 4, corresponding to 60–65% exchange (*8*).

The zeolite samples were first activated by heating under continuous vacuum to 450°C. The surface was considered sufficiently dehydrated when the O—H stretch at 3650 cm^{-1} had negligible intensity. The dehydrated CuNaY contains both Cu(I) and Cu(II) and will be denoted as Cu(I,II) NaY (*9*). It is likely that the exchanged Fe(II)NaY contains some Fe(III), but since it is known that Fe(III) in zeolite can be reduced to Fe(II) upon heating-dehydration treatment (*10*), the Fe ions in our Fe(II)NaY sample after dehydration treatment were mostly in the Fe(II) state. To prepare Fe(III)NaY and Cu(II)NaY, the dehydrated samples were treated with oxygen (400 Torr) at 450°C for 0.5 hr and then evacuated until the pressure read below 10^{-4} Torr. Each sample was treated with oxygen three times. To check the oxidation states

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and the concentrations of Fe in FeNaY before and after pyrrole adsorption, the 1,10-phenanthroline complexation method (*11*) was used. The absorbance of the iron–phenanthroline complex was measured on a Cary 118 spectrophotometer. The dehydrated sample after oxygen treatment was found to have 99.7% of the total iron concentration in the Fe(III) state.

In situ transmission IR studies were carried out using a short path length glass cell (*12*). A 10-mg finely ground zeolite sample (NaY, CuNaY, or FeNaY) was pressed to a thin wafer at 20,000 psi for 2 min in a stainless-steel die. The wafer was activated by heating under vacuum to 450°C for 4 h. Pyrrole (Aldrich, 98% pure) was vacuum-distilled prior to use. The purified pyrrole was adsorbed onto zeolite samples at room temperature via a vacuum line at pressure readings of 0.1 to 9 Torr. All IR spectra of the wafers were taken on a Perkin–Elmer 283 spectrophotometer.

Zeolite powder samples were activated and treated with pyrrole using the same procedure as that used for the wafers. The pyrrole-treated sample was then evacuated for 3 h and stored under vacuum until they were used for surface area determination, FTIR, NMR, ESR, and conductivity measurements. FTIR spectra of the powder samples were recorded on a Nicolet 20SXB spectrometer with a DRIFT accessory; KBr was used as a reference. ^{13}C NMR spectra of solids were recorded on a Nicolet NT-150 wide-bore spectrometer using magic angle spinning and cross polarization (*13*). ESR spectra were recorded on a Varian E-3 spectrometer. Conductivities of powder samples were measured by the standard four-probe method under vacuum. The powder sample was vacuum-pressed at 100°C and 35,000 psi to a compact of 2.5 cm in diameter.

The adsorption and desorption behavior of pyrrole on the Fe(II)NaY and Fe(III)NaY, Cu(I,II)NaY, and Cu(II)NaY zeolites was monitored by *in situ* transmission IR spectroscopy on wafer samples. NaY was also studied, as a reference. Figure 1 shows the IR spectra of liquid pyrrole and of Fe(II)NaY and Fe(III)NaY before and after pyrrole adsorption. Figure 2 illustrates the spectra of Cu(I,II)NaY and Cu(II)NaY before and after pyrrole adsorption. In Fig. 3, the spectra of NaY before and after pyrrole adsorption as well as after desorption at 150°C for 2 h are included. Adsorption of pyrrole on NaY, Fe(II)NaY, and Cu(I,II)NaY gave almost identical results. The IR spectra of these pyrrole adsorbed surfaces (Figs. 3b, 1c, and 2b) are very similar in peak positions as well as relative intensities. Overall, all three spectra showed very little difference from the spectrum of liquid pyrrole. The only noticeable changes are with the two broad peaks of liquid pyrrole at 1715 and 1575 cm^{-1} which appear at slightly shifted wavenumbers on the zeolite surfaces. These peaks are present even in purified pyrrole and are usually attributed to traces of oligomer impurities. The intensities of all the peaks due to adsorbed pyrrole on NaY diminished significantly after desorption treatment (Fig. 3), and after further heating and evacuation, only a few peaks of very low intensity remained. Cu(I,II)NaY and Fe(II)NaY gave identical desorption behavior as the NaY. It is therefore concluded that pyrrole adsorbed similarly on Fe(II)NaY, Cu(I,II) NaY, and NaY, with predominantly physical adsorption on the zeolite. Pyrrole adsorption did not impart any immediate color changes to NaY, Fe(II)Y, or Cu(I,II)Y.

Pyrrole adsorbed on Fe(III)NaY, however, gave entirely different results. Fe(III)NaY underwent dramatic color changes upon pyrrole adsorption. It turned from rust orange to green at low concentrations of pyrrole (0.02 Torr, 1 s adsorption time) then to royal blue and finally to black after 2 min of exposure time at 9 Torr of pyrrole. The reaction rate was extremely rapid as indicated by instantaneous color changes upon pyrrole adsorption. It was found by the 1,10-phenanthroline method

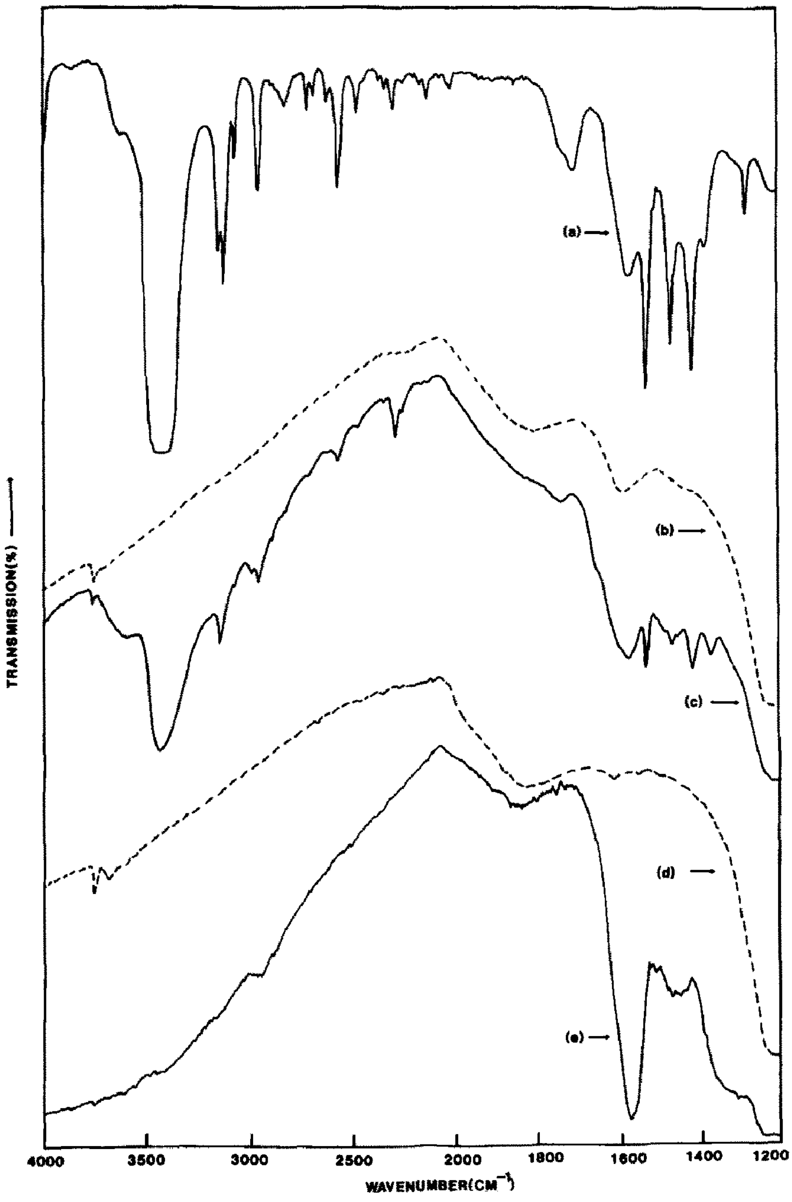

FIG. 1. Transmission infrared spectra of pyrrole- and iron-exchanged NaY zeolite before and after pyrrole adsorption. (a) Liquid pyrrole. (b) Fe(II)NaY zeolite, dehydrated under vacuum for 4 h at 450°C. (c) Fe(II)NaY zeolite (sample from (b)) after pyrrole adsorption. (d) Fe(III)NaY zeolite, dehydrated as in (b) followed by oxygen treatment. (e) Fe(III)NaY zeolite (sample from (d)) after pyrrole (0.02 Torr and 1 s) adsorption.

that, after pyrrole adsorption, 91.9% of the iron in the zeolite sample was Fe(II), indicating an almost complete reduction of Fe(III) to Fe(II), which is also indicated by the accompanying color change of the surface. Therefore, formation of polymer of pyrrole through oxidative coupling of pyrrole units is likely to have occurred.

Adsorption of pyrrole on Fe(III)NaY zeolite powder sample showed that a maximum of 3.2 g of pyrrole was adsorbed on 16.1 g of zeolite, which gives approximately

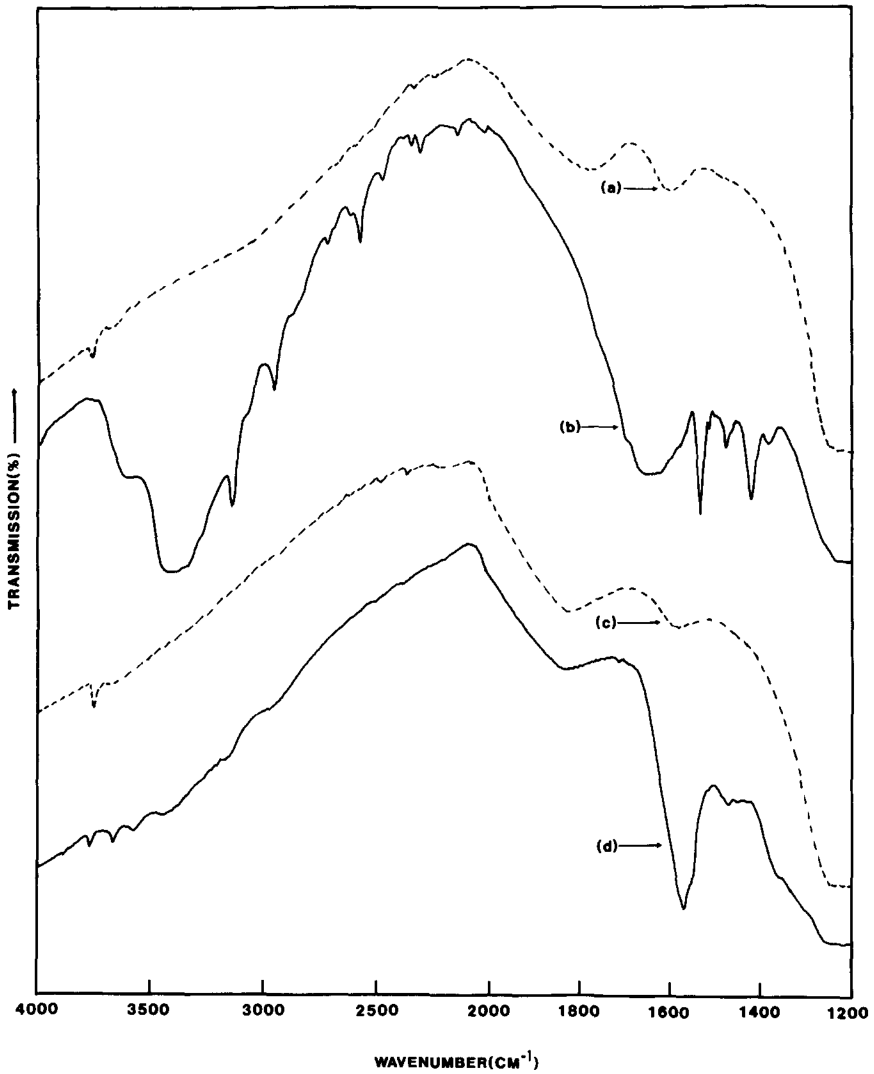

FIG. 2. Transmission infrared spectra of copper-exchanged NaY zeolite before and after pyrrole adsorption. (a) Cu(I,II)NaY zeolite, dehydrated under vacuum for 4 h at 450°C. (b) Cu(I,II)NaY zeolite (sample from (a)) after pyrrole (9 Torr, 10 min) adsorption. (c) Cu(II)NaY zeolite, dehydrated as in (a) followed by oxygen treatment. (d) Cu(II)NaY zeolite (sample from (c)) after pyrrole (0.01 Torr and 1 s) adsorption.

five pyrrole molecules per supercage. The surface area of the zeolite was found to have been reduced to 12.0 m^2/g after pyrrole adsorption. A desorption study of the pyrrole chemisorbed zeolite sample was carried out by heating the wafer to 150°C under vacuum for 2 h; the IR spectrum showed no change. We also attempted to desorb the product using a variety of polar and nonpolar solvents: water, chloroform, toluene, carbon tetrachloride, hydrochloric acid (3 *M*), hydrochloric acid (concd), and sodium hydroxide (3 *M*). After extraction, the organic solvent was evaporated almost to dryness and an IR spectrum was taken on the residue. When aqueous solutions were used, the solution was first shaken with toluene and then the organic layer was

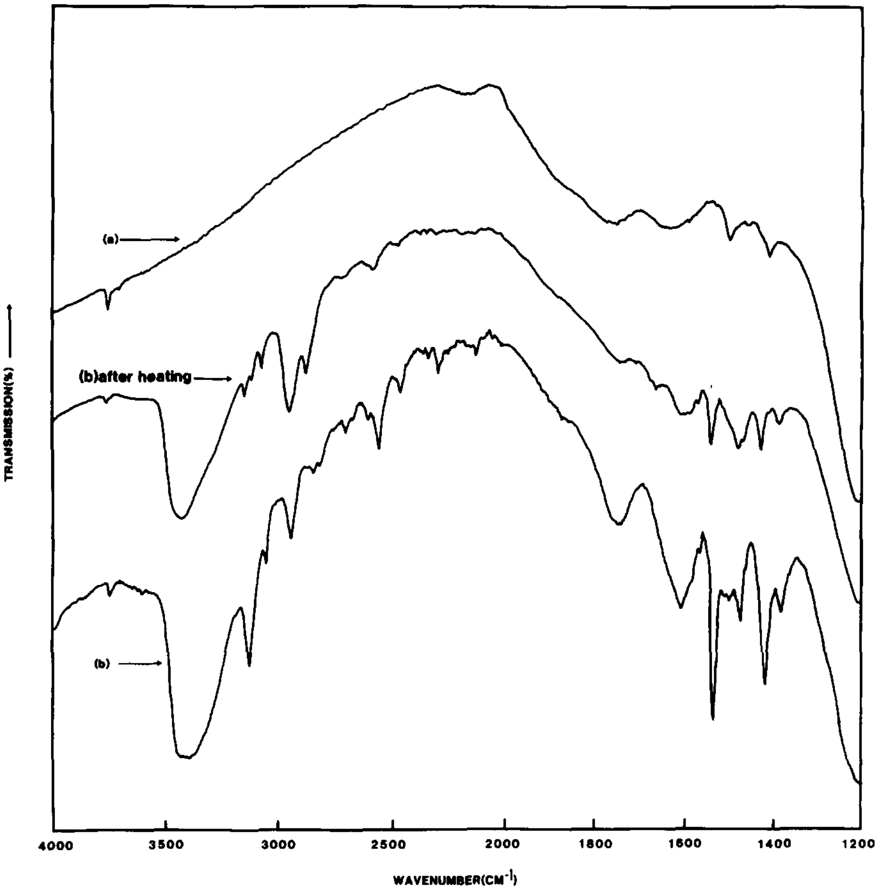

FIG. 3. Transmission infrared spectra of NaY zeolite before and after pyrrole adsorption and after desorption treatment. (a) NaY zeolite, dehydrated under vacuum for 4 h at 450°C. (b) NaY zeolite (sample from (a)) after pyrrole (9 Torr, 10 min) adsorption. (b) After heating: the sample from (b) was heated under continuous vacuum for 2 h at 150°C.

concentrated and subsequently examined. No organic matter other than the extracting solvent was detected by IR in any of the above experiments. This result is consistent with the assumption that the product is polymeric and because of its size the product cannot leave the supercage of the zeolite.

The IR spectrum of pyrrole-adsorbed Fe(III)NaY (Fig. 1e) gives a broad and strongly absorbing band from 4000 to 2000 cm^{-1}, an extremely intense peak at 1562 cm^{-1} and several weaker peaks in the region 1530–1350 cm^{-1}. We compared our IR spectrum to that of the pyrrole oligomers and polymers: 2,2′-bipyrrole (*14*), pyrrole trimer (*7*), acid-synthesized polymer (*6*), electrochemically synthesized polypyrrole perchlorate (PP$^+$ClO$_4^-$), and the reduced neutral polypyrrole (*15*). Among all the species compared, PP$^+$ClO$_4^-$ has an IR spectrum which closely resembles the spectrum of our product. Both exhibit a strongly absorbing background in the region 4000–2000 cm^{-1} and, in addition, the normally intense N—H stretching mode at 3410 cm^{-1} is rather unpronounced and the CH stretches are almost absent. The only major difference is in the intensity of our peak at 1562 cm^{-1} in comparison to the highest en-

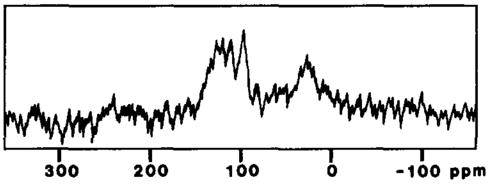

FIG. 4. ^{13}C NMR spectrum of Fe(III)NaY zeolite powder after pyrrole (9 Torr, 50 min) adsorption.

ergy ring vibration peak in $PP^+ClO_4^-$. Since both polymers resulted from oxidative coupling of pyrrole units, it is reasonable to expect that their structures are quite similar. Our IR spectrum does show new peaks at 3650 and 3554 cm^{-1} as illustrated in Figs. 1e and 2d. This indicates the formation of OH's on the zeolite surface probably resulting from the addition of abstracted H^+ (from pyrrole) to Si—O—Al of zeolite framework or to nonframework oxygen.

The peak at 1562 cm^{-1} is the most dominant and interesting peak in our spectrum. It is considerably narrower and much more intense than the 1580-cm^{-1} peak in the spectra of pyrrole-adsorbed Fe(II)NaY and Cu(I,II)NaY. $PP^+ClO_4^-$ has a peak at 1540-cm^{-1} but not nearly as intense as our 1562-cm^{-1} peak. There are several possible assignments for this intense peak. Based on its frequency, it can be assigned to the highest energy pyrrole ring stretch of polypyrrole. However, we could not account for its unusual intensity. It could also be due to the NH bending of a partially saturated product; however, it is known that such peaks are usually extremely weak. If we assume that some of the abstracted H^+ were added to the NH group and not to the ring itself, we can assign this peak to NH_2^+ bending. Even though pyrrole is a very weak base, the presence of salt in the form of $\rangle NH_2^+Cl^-$ was detected in crytopyrrole hydrochloride and an intense peak at 1575 cm^{-1} was assigned to NH_2^+ bending (*16*). We, therefore, propose that the polymeric product is probably in a cationic state with H^+ associated with the pyrrole's N to form NH_2^+ and becomes an integral part of the zeolite. The much weaker peaks in the region 1530–1350 cm^{-1} are probably due to other ring vibrations of the polymer. In conclusion, our IR data indicates that the product is mostly oxidatively coupled polypyrrole in the cationic form, and there is no evidence for the existence of nonaromatic C=C. Diffuse reflectance IR spectra obtained for all the above samples in the powder form gave identical information as the transmission IR spectra of the wafers.

The ^{13}C NMR spectrum of the Fe(III)NaY zeolite powder after pyrrole is shown in Fig. 4. Three broad peaks were observed. The chemical shifts of the peaks measured down field from TMS are: 123 ppm with a shoulder at 107, 97, and 31 ppm. The peak at 123 ppm, with its overlapping shoulder at 107 ppm, can be assigned to the α and β carbons of pyrrole units (*17*). The peak at 97 ppm could be due to nonaromatic C=C in a ring or in ring-opening products. In their work with $PP^+ClO_4^-$, Street *et al.* assigned the peak at 135 ppm as due to non-α,α'-linkages of pyrrole polymer (*15*). The absence of a peak around 135 ppm in our spectrum suggests that most of our pyrrole units are α,α'-linked. The peak at 31 ppm can be assigned to alkane-type carbons of some decomposition products.

The ESR spectrum of Fe(III)NaY zeolite after pyrrole adsorption (Fig. 5) was taken at room temperature in air. The spectrum has a singlet peak with $g = 2.0026$ and $\Delta H = 16$ G. (The g value was measured relative to DPPH.) The concentration of the paramagnetic species was found to be 1×10^{18} spins/g of zeolite. After storing the sample in air for one month, the peak intensity reduced to approximately 70% of the original spectrum but the width remained unchanged. The spectrum is most likely due to the pyrrole polymer product formed on the zeolite surface which is known to be a good stabilizing matrix for free radicals. We ruled out the possibility of unreacted Fe(III) ions after comparing our spectrum

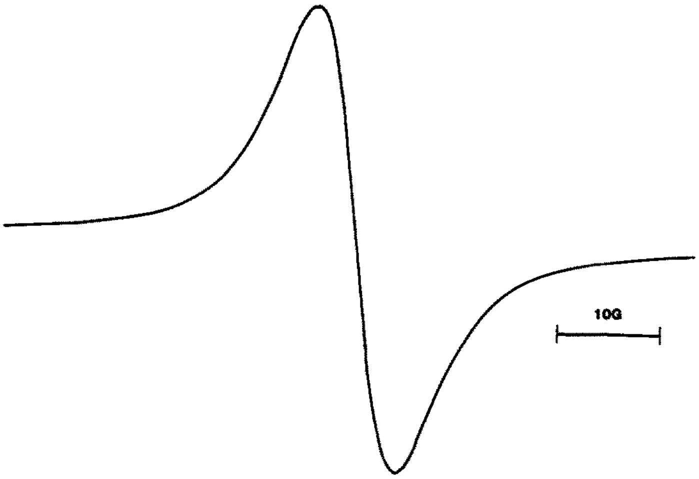

FIG. 5. ESR spectrum of Fe(III)NaY zeolite powder after pyrrole (9 Torr, 50 min) adsorption.

with the spectrum obtained from a study of iron-exchanged zeolite by Wichterlova (*18*). This absence of Fe(III) ion on the zeolite after pyrrole adsorption is in good agreement with the result of our chemical analysis. Our ESR peak is not due to simple pyrrole radicals either. It lacks the hyperfine structure of the spectra reported for pyrrole radicals formed from hydrogen addition, hydrogen abstraction (*19*), and one-electron reduction of pyrrole (*20*).

Cu(II)NaY reacted similarly as Fe(III) NaY toward adsorbed pyrrole. By comparing Figs. 1e and 2d, it is evident that pyrrole adsorbed on Cu(II)NaY wafer gave an identical product as pyrrole on Fe(III)NaY. The color of Cu(II)NaY sample changed from green to dark blue then black upon pyrrole adsorption which also resembled the behavior of Fe(III)NaY. The product on the zeolite surface also could not be desorbed by heat or solvents. As discussed earlier, Cu(I,II)NaY does not promote the polymerization reaction even though there are Cu(II) ions in the sample. This could be due to the fact that these Cu(II) ions are located in sites which are not readily accessible to pyrrole molecules.

Since spectroscopic evidence suggests that our polypyrrole might be quite similar to the electrically conducting polypyrroles, we had hoped that the pyrrole-adsorbed Fe(III)NaY zeolite could be conducting as well. The compressed disk of pyrrole adsorbed Fe(III)NaY zeolite powder gave a conductivity of 4.60×10^{-12} S/cm. Doping the sample with Br_2 vapor for 0.5 hour did not improve the conductivity significantly. The electrical conductivity of the compressed powder lies in the insulating range, similar to the untreated Fe(III)NaY. Most likely the concentration of polypyrrole in zeolite is not high enough to dominate the electrical properties of the mixture.

In conclusion, we have found that Cu(II)NaY and Fe(III)NaY oxidized and converted adsorbed pyrrole into a colored, cationic radical polymeric product. The reaction is extremely rapid. Zeolite samples with nonoxidative cations (Na, Cu(I), Fe(II)) can adsorb pyrrole as well, but the adsorption is physical in nature. The products formed on Fe(III) and Cu(II)-exchanged NaY zeolites are identical, which leads one to believe that Fe(III) and Cu(II) ions play the same role in this reaction as the oxidant. The product probably consists mostly of straight chain cationic polymer of pyrrole resulting from dehydrogenation at the α-carbons and becomes an integral part of the zeolite system. Results of this study indicate that rapid formation of oxidatively coupled polymers could be one of the important mechanisms that are responsible for the poisoning effect of pyrroles on Y zeolite, because it is known that a catalyst will lose its activity if the active sites are covered by polymers. In addition, our results have also shown that Fe(III)NaY and Cu(II)NaY zeolites are potentially good candidates to effectively remove pyrrole-type impurities in shale-derived fuel by pyrrole chemisorption on the zeolite.

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