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# Pyrrole oligomerization within H–Fe–FAU zeolite

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We have investigated the possibility of pyrrole oligomerization within zeolite channels in acid zeolites containing $Fe^{3+}$ to study the action of acid and one-electron oxidation polymerization mechanisms together. We also indicate the possibility of preparing materials with electrical conductivities varying within a wide range based on the combined adsorption of pyrrole and water in acid zeolites. Further it is shown that pyrrole polymerization is possible at the surface of amorphous aluminosilicates with the consequent generation of a hydrophobic surface.

## 1. Introduction

In organic polymers where there exists a regular alternation of single and double bonds (acetylene, polypyrrole, polytiophene, polyaniline etc.), the $\pi$-electron system develops a molecular orbital which extends throughout the polymer chain. The material obtained could be described to a first approximation by a fully occupied valence band and an empty conduction band formed by $\pi$ and $\pi^*$ systems, respectively; in this state the materials are semiconductors. The injection of holes and electrons into these chains by proper functionalization leads to p-type or n-type conduction. [1–4].

The encapsulation of conducting polymer chains in low-dimensional ordered host lattices like zeolites is an interesting way to obtain charge-carrier confinement [5], providing a mechanism for functionalization via the charge-compensating cations present in zeolite cavities and channels and to induce different polymerization pathways [6–10].

The first studies on the formation of conducting polymers in zeolites were made during the investigation of pyrrole adsorption in $Fe^{3+}$- and $Cu^{2+}$- exchanged Y zeolite [11]. The synthesis of polypyrrole as potential "molecular wires" within Y zeolite and Mordenite was recently reported too [12].

In previous reports on the polymerization of pyrrole within zeolite channels the mechanism for this process was one-electron oxidation of pyrrole, which leads to polypyrrole resulting from linking of the monomers in the $\alpha$-position [7, 11, 12].

We have investigated the possibility of pyrrole oligomerization within zeolite channels in acid zeolites containing $Fe^{3+}$ to study the action of acid and one-electron oxidation polymerization mechanisms together.

## 2. Experimental procedure

Zeolite Na–FAU (Si/Al = 1.25) was obtained from Laporte; it was exchanged to $NH_4$–FAU by refluxing five times during 4 h at 373 K with a 1 M solution of $NH_4Cl$. $Fe^{3+}$ was added by dropping at 300 K a 0.1 M solution of $Fe_3Cl$ into $NH_4$–FAU, obtaining finally a sample ($NH_4$–Fe–FAU) with the following cationic composition: $NH_4^+ = 4.2\ \mathrm{meq\,g^{-1}}$, $Fe^{3+} = 1.3\ \mathrm{meq\,g^{-1}}$ and $Na^+ = 0.3\ \mathrm{meq\,g^{-1}}$, determined by atomic absorption (SP 1900 Pye Unicam spectrometer).

The sample obtained was thermally treated at two temperatures, 750 and 600 K. After the treatment the X-ray diffractograms (TUR M62 Carl Zeiss powder diffractometer, $CuK_\alpha$ radiation) of both samples were taken with the following results: the sample treated at the higher temperature was completely amorphous (its label will be AF) and that treated at the lower temperature was crystalline (H–Fe–FAU).

The surface area of the amorphous powder was $150\ \mathrm{m^2\,g^{-1}}$ (determined by the BET method in a Carlo Erba sorptiometer).

Pyrrole was allowed to diffuse in a vacuum ($10^2$ Pa) into H–Fe–FAU cavities and pores containing $H^+$ and $Fe^{3+}$ ions as charge-compensating cations, and over the surface of AF, in both cases at 300 K. The samples obtained after pyrrole adsorption will be named (PPY)H–Fe–FAU and (PPY)AF. Both samples were allowed to adsorb water before the characterization.

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The characterization of the material prior to and after pyrrole adsorption was carried out with the help of i.r. spectrometry using the KBr disc technique in a Philips PU 9800 FT-IR spectrometer and a Philips PU 9512 IR spectrometer, and $^{57}$Fe Mössbauer spectrometry in a Wissel constant-acceleration spectrometer with $^{57}$Co in Rh matrix source at room temperature. Sample thickness was calculated to obtain an iron surface density of around 15 mg cm$^{-2}$. A REM computer program [13] based on Gauss–Newton methods was used for spectra resolution and parameter determination (isomer shift $\delta$ relative to sodium nitroprussite, quadrupole splitting $\Delta$ and relative area $A$). Further, differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out in an MOM Q-1500-D Derivatograph with a rate of temperature increment of 5 K min$^{-1}$, a final temperature of 773 K and 158 mg of sample in the holder. Thermodielectric analysis was carried out in equipment developed by us which is described elsewhere [14], where the impedance of cylindrical capacitors filled with the sample and a reference ($Al_2O_3$) during the linear scanning of temperature from 300 to 1273 K are compared.

## 3. Results and discussion

The first fact easily noted in all samples after pyrrole adsorption is the colour change which turns the powder surface black. This is qualitative evidence of the oligomerization of pyrrole during its adsorption.

The FT-IR spectrum of (PPY)H–Fe–FAU shows as the most noticeable features two bands at 1712 and 1563 cm$^{-1}$. In Fig. 1 both bands appear in the difference spectrum obtained from the spectra of (PPY) H–Fe–FAU and H–Fe–FAU, which are shown too. Both bands are ascribed to pyrrole oligomers [11] and the band at 1563 cm$^{-1}$ is also reported for bulk and encapsulated polypyrrole [12] with a slight difference in position. In sample (PPY)AF (Fig. 2) the same absorption i.r. bands are present. The presence of these bands in the i.r. and FT-IR spectra of both kinds of sample, i.e. amorphous and crystalline, is a consequence of the polymerization of pyrrole at the surface of AF and in the cavities of H–Fe–FAU. [11, 12] The band at 1563 cm$^{-1}$ could be assigned to $NH_2^+$ bending. This result allows us to propose that the polymeric product is in a cationic state with protons associated with the pyrrole NH group to form $NH_2^+$, which becomes a charge-compensating cation of the zeolite [11].

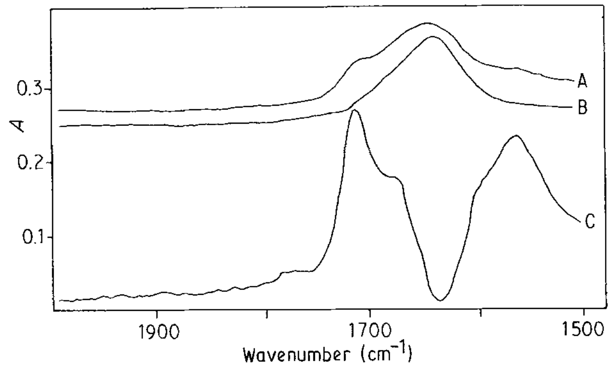

*Figure 1* FT-IR spectra of the samples: (A) (PPY) H–Fe–FAU, (B) H–Fe–FAU, (C) 9 × [(PPY)–H–Fe–FAU–H–Fe–FAU].

The parameters of the Mössbauer spectra of samples (PPY)H–Fe–FAU and H–Fe–FAU are reported in Table I. These parameters correspond to octahedrally coordinated Fe$^{3+}$ [13, 15] with no traces of Fe$^{2+}$, i.e. there is no evidence of the one-electron oxidation polymerization mechanism of pyrrole in these samples. The results reported above indicate that in the present case acid polymerization is the preponderant mechanism for the formation of polypyrrole chains (Fig. 3). The polypyrrole chain could be in cationic form as indicated in Fig. 3 or could be neutral, i.e. the proton returns to the zeolite cationic positions or there could be a dynamic process of equilibrium between the neutral and the cationic form.

The TGA shows that the sample (PPY)H–Fe–FAU contains 1.2 mmol g$^{-1}$ of adsorbed pyrrole, i.e. about

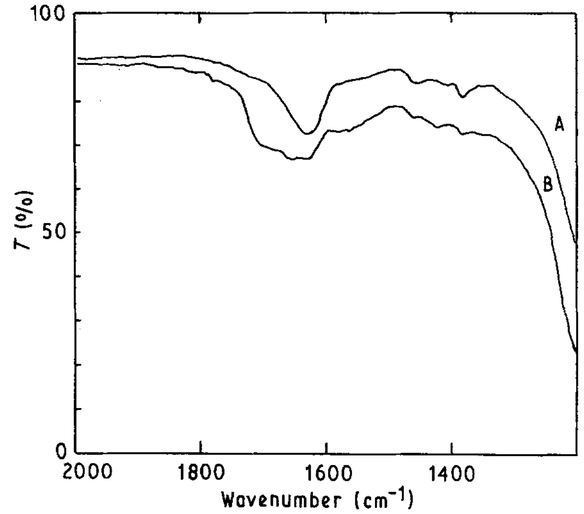

*Figure 2* I.r. spectra of the samples: (A) AF, (B) (PPY) AF.

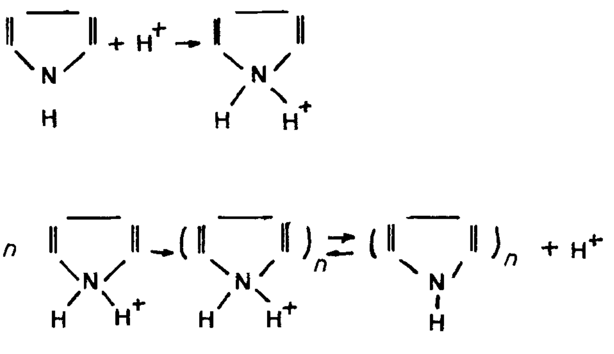

*Figure 3* Schematic representation of the acid mechanism of pyrrole polymerization in zeolites.

TABLE I Mössbauer parameters of (PPY)H–Fe–FAU and H–Fe–FAU.

| Sample | $\delta$ (mm s$^{-1}$) | $\Delta$ (mm s$^{-1}$) | $A$(%) |
|---|---|---|---|
| (PPY)H-Fe-FAU | 0.621 | 1.023 | 100 |
| H-Fe-FAU | 0.616 | 1.022 | 100 |

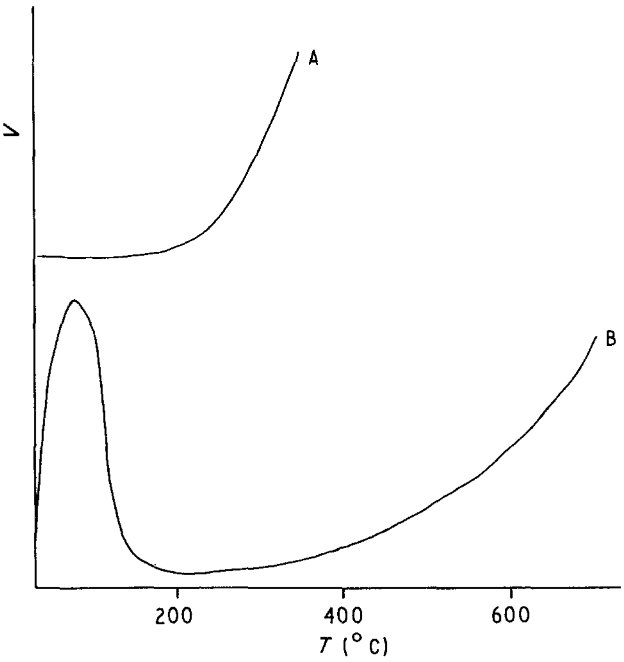

*Figure 4* Thermodielectric thermograms of the samples: (A) (PPY)H–Fe–FAU, (B) H–Fe–FAU.

two pyrrole molecules per cavity and 9.9 mmol $g^{-1}$ of water. This means that about 30% of the zeolite cavity is occupied by polypyrrole chains and the rest by water.

The thermodielectric thermograms of (PPY)AF and AF are reported in Fig. 4. The thermograms show the low-temperature peak corresponding to water and cationic polarization for AF and the absence of this effect for (PPY)AF [16, 18]. This fact indicates that water is not detectable in the (PPY)AF sample by thermodielectric analysis, i.e. the adsorption of pyrrole in AF generates a hydrophobic surface (its surface area measured by the BET method is 40 $m^2 g^{-1}$).

The conductivity of compacts prepared with the powder corresponding to sample (PPY)H–Fe–FAU was $\sigma = 1.2 \times 10^{-7}$ S $m^{-1}$ and for $NH_4$–Fe–FAU, $\sigma = 3 \times 10^{-5}$ S $m^{-1}$ [19]. The value determined by other authors [11] for compacts without water adsorbed in the zeolite channels is $\sigma = 4.6 \times 10^{-14}$ S $m^{-1}$. This fact is directly related to the presence of water in our samples which provides an efficient mechanism for cationic conduction [18, 20, 21]. The figures reported for the measured conductivities indicate that in the case of polypyrrole chains with an occupation of 4–5 molecules per cavity and no water included in the zeolite the material behaves as an insulator, i.e. the polymer did not form unbroken continuous strands traversing entire zeolite crystallites [11, 12] ; in the case of two pyrrole molecules per cavity, i.e. 30% of the zeolite occupied by polypyrrole chains and the rest by water, the measured conductivity is seven orders of magnitude higher, and finally in the original sample (without pyrrole) nine orders of magnitude higher.

These results indicate the possibility of preparing materials with electrical conductivities varying within wide ranges based on the combined adsorption of pyrrole and water in acid zeolites. On the other hand, it was shown that pyrrole polymerization is possible at the surface of amorphous aluminosilicates with the consequent generation of a hydrophobic surface.

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## References

1. H. SHIRAKAWA, E. LOUIS, A. MACDIARMID, C. CHIANG and A. J. HEEGER, *J. Chem. Soc. Chem. Commun.* (1977) 758.
2. G. TOURILLON and F. GARNIER, *J. Electroanal. Chem.* **135** (1982) 173.
3. A. G. MACDIARMID, J. C. CHIANG, M. HALPERN, W. S. HUANG, S. L. MU, N. D. L. SOMASIRI, W. WU and S. YANIGER, *Mol. Cryst. Liq. Cryst.* **121** (1985) 173.
4. F. GARNIER, *Angew. Chem.* **101** (1989) 529.
5. G. A. OZIN, A. KUPERMAN and A. STEIN, *ibid.* **101** (1989) 3731.
6. P. ENZEL and T. BEIN, *J. Phys. Chem.* **93** (1989) 6270.
7. J. V. CASPAR, V. RAMAMURTHY and D. CORBIN, *J. Amer. Chem. Soc.* **113** (1991) 600.
8. D. R. ROLISON, *Chem. Rev.* **90** (1990) 867.
9. P. ENZEL and T. BEIN, *J. Chem. Soc. Chem. Commun.* (1989) 1326.
10. P. BEIN and T. ENZEL, *Synth. Met.* **29** (1989) 163.
11. T. H. CHAO and H. A. ERF, *J. Catal.* **100** (1986) 492.
12. T. BEIN and P. ENZEL, *Angew. Chem.* **28** (1989) 1692.
13. R. ROQUE, C. DIAZ, E. REGUERA, J. FUNDORA, L. LOPEZ and M. HERNANDEZ, *Zeolites* **10** (1990) 685.
14. A. MONTES, R. ROQUE and E. D. SHCHUKIN, *J. Thermal Anal.* **31** (1986) 41.
15. C. DE LAS POZAS, C. DIAZ, E. REGUERA and R. ROQUE, *J. Solid State Chem.* **93** (1991).
16. R. ROQUE and A. MONTES, *J. Thermal Anal.* **31** (1986).
17. M. CARRERAS, R. ROQUE and C. DE LAS POZAS, *ibid.* **32** (1987) 1271.
18. R. ROQUE and M. HERNANDEZ, *ibid.* **36** (1990) 1025.
19. O. VIGIL, M. HERNANDEZ, J. FUNDORA, J. DE OÑATE and R. ROQUE, in preparation.
20. R. ROQUE and M. HERNANDEZ, *J. Thermal Anal.* **36** (1990) 2024.
21. O. VIGIL, M. HERNANDEZ, J. FUNDORA, H. VILLAVICENCIO and R. ROQUE, *J. Mater. Sci. Lett.* in press.

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