

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, polythiophene, polyaniline etc.), the π -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 π and π^* 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 α -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 ($\text{Si}/\text{Al} = 1.25$) 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: $\text{NH}_4^+ = 4.2 \text{ meq g}^{-1}$, $\text{Fe}^{3+} = 1.3 \text{ meq g}^{-1}$ and $\text{Na}^+ = 0.3 \text{ meq g}^{-1}$, 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_α 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 $150 \text{ m}^2 \text{ g}^{-1}$ (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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