

ENCAPSULATION OF POLYANILINE IN ZEOLITE Y AND MORDENITE

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ABSTRACT

Synthetic strategies to encapsulate polyaniline in the crystalline channel system of faujasite (three-dimensional) and mordenite (one-dimensional) have been explored. The adsorption of anilinium precursor into the zeolite host and its successful oxidation to polyaniline have been studied utilizing FTIR, Fourier Transform Raman, and electronic spectroscopies. The dimensionality of the host channel system and the concentration of hydroxyl groups present influence the nature of the intrazeolite polymerization products.

INTRODUCTION

The successful development of models for the interpretation of physical properties of conducting polymers depends upon well-defined, structurally known systems. In an approach to address the problem of structural definition, our research efforts are directed at the stabilization or encapsulation of polymeric chain conductors in low-dimensional, crystalline host lattices such as zeolites. This communication reports recent results on the encapsulation of polyaniline in different zeolite channel structures.

Chemical or electrochemical^{1,2} oxidative polymerization of aniline in aqueous acid solution yields the 'emeraldine salt' form of polyaniline (PANI), which is believed to have approximately the following 1:1 amine-to-imine composition:³



where A⁻ is an anion. Depending upon the fractional content of amine vs. imine nitrogen, the different forms of polyaniline range from leuco-emeraldine (only amine) to pernigraniline (only imine). Partially oxidized forms containing imine nitrogens can be doped by nonoxidizing protonic acids, thus transferring positive charge to the backbone. The zeolite hosts are an important part of the nanocomposites under study. Zeolites are open framework oxide structures (classically aluminosilicates with hydrophilic surfaces) with pore sizes between 0.3 and 0.8 nm and exchangeable cations compensating for the negative charge of the framework^{4,5}. The host structures examined in this study include zeolite Y, composed of sodalite cages (0.3 nm windows) interconnected by double six-rings of Si/Al and of 'supercages' with 0.8 nm windows which together form a 3-D open framework, and mordenite (MOR) featuring pseudo-one-dimensional twelve-ring channels.

The intrazeolite PANI has been characterized using a combination of vibrational and electronic spectroscopies. In particular, Fourier Transform Raman experiments^{6,7,8} allowed us to study low energy vibrations of the polymer backbone which are weak in the IR and obscured

by the strong lattice modes of the zeolite host. This new Raman technique is aimed primarily at elimination of the fluorescence problem. Excitation in the near infrared is combined with light sampling in an interferometer.

EXPERIMENTAL

The Na and NH₄ forms of zeolite Y (LZY-52, LZY-62; FAU) and the Na form of MOR (LZM-5) were obtained from Union Carbide, the other chemicals from Aldrich. The proton form of FAU (HY) was prepared by deamination of NH₄Y under vacuum at a rate of 1 K/min to 720 K and holding at 720 K for 10 h. The proton form of MOR (HMOR) was obtained by stoichiometric ion exchange with HCl. The zeolites were ion exchanged with aniline hydrochloride in aqueous suspension and subsequently oxidized with ammonium peroxodisulfate under stirring for 12 h (Table 1). Extraction of the zeolite/PANI samples with DMSO removed between 30 and 50% of the polymer as indicated by electronic spectra. This fraction appeared to be located at the surface of the zeolite crystals. Only minor changes in the spectroscopic properties of the remaining, intrazeolite PANI were observed. FTIR spectra were taken at 4 cm⁻¹ resolution with a Mattson Polaris instrument and were processed with ICON software. Electronic spectra were obtained with a PE 356 spectrophotometer. The instrumentation for Fourier Transform Raman spectroscopy was a combination of a near-infrared interferometer with a 5 W Nd:YAG laser (1064 nm, Spectron), and an optical arrangement for sample irradiation and signal collection⁹.

Table 1. Composition of PANI-Loaded Zeolites.

Sample Name	Zeolite Composition	H-Aniline Content	Oxidant Ratio
PANI (Bulk)	--	--	1:4
NaY/P28	Na ₅₇ (AlO ₂) ₅₇ (SiO ₂) ₁₃₅] 240 H ₂ O	28/u.c.	1:4
H45Y/P36	H ₄₅ Na ₁₀ [(AlO ₂) ₅₅ (SiO ₂) ₁₃₇] 240 H ₂ O	36/u.c.	1:4
NaMOR/P6	Na ₈ [(AlO ₂) ₈ (SiO ₂) ₄₀] 24 H ₂ O	6.1/u.c.	1:4
HMOR/P6	H ₈ [(AlO ₂) ₈ (SiO ₂) ₄₀] 24 H ₂ O	6.0/u.c.	1:4

RESULTS AND DISCUSSION

Identification of polyaniline reaction products

The most striking effect of adding the peroxodisulfate oxidant to the white suspension of acid anilinium zeolites is the gradual change of color to deep blue. This reaction proceeds during a few hours at room temperature and strongly resembles the oxidation of anilinium in homogeneous phase.¹⁰ However, the reaction of anilinium in solution under similar overall conditions of temperature and concentrations is completed within a few minutes. In comparison, this behavior suggests that polymerization of anilinium can indeed take place in zeolites and that

the reaction rate is much slower because the oxidant has to diffuse into the zeolite channel system.

The following spectroscopic data strongly support this hypothesis. The electronic spectrum of the blue sample HMOR/P6 shows a rather strong absorption beginning at about 460 nm, growing into a weak shoulder at 590 nm, a maximum at 745 nm, and extending into the near infrared (Figure 1). This absorption is not present in either the acid zeolite or the anilinium loaded precursor (both are white). The sodium containing sample NaMOR/P6 has a similar absorption in the red but a weaker shoulder at 590 nm. A comparison between acid and sodium Y zeolite anilinium samples reveals similar trends but the red absorption extends further into the infrared than that of the MOR samples (Figure 1). If bulk PANI, obtained from oxidation of anilinium in HCl, is extracted with DMSO, the blue solution exhibits a strong band at 600 nm which is assigned to the free base polymer¹¹ (Figure 1). It is suggested that the different electronic absorptions are related to PANI forms of different chain lengths and/or levels of protonation. Based upon the electronic spectra, in all zeolite samples the emeraldine salt form of PANI has been synthesized as shown by the strong absorption beyond 800 nm and the minimum at 500 nm¹¹. In addition, small fractions of the free base polymer are indicated by the presence of the shoulder at 590 nm. As the absorption of H45Y/P36 is more red shifted than that of the MOR samples, the polymerization appears to be favored in the larger pore 3-D network of Y zeolite. It can be assumed that the access of oxidant is less hindered in this host.

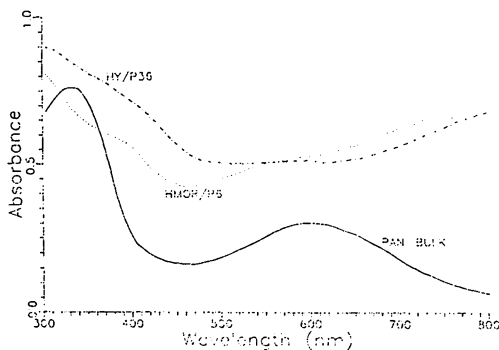


Fig. 1. Electronic spectra of sample HMOR/P6, sample H45Y/P36, and bulk PANI.

Extraction experiments with DMSO showed that the sodium zeolite samples lost a significantly higher polymer fraction than the acid samples. The electronic spectra of the

filtrates indicate enrichment of the free base polymer. If the excess of protons available in the acid zeolites protonates the polymer more completely than in the sodium zeolites, it can be assumed that those protonated polymers are more efficiently retained in the highly polar environment of the zeolite.

Fourier transform Raman spectra of the two acid samples HMOR/P6 and H45Y/P36 excited at 1064 nm show remarkable broad emission features which extend almost over the entire instrument response range. These features are assigned to fluorescence of the samples which are excited at an energy of considerable electronic absorption. In addition to the broad-band emission, both samples show similar Raman lines (Figure 2) which correspond well to those observed of bulk PANI in conventional Raman scattering with excitation at 647.1 and 632.8 nm.^{12,13} These include a set of five bands between 1200 and 1600 wavenumbers which correspond to CCH bending and CC/CN' stretching modes of the benzoic and quinoinic structure of the polymer backbone. Since several of these Raman lines do not correlate with those of aniline hydrochloride (1275, 1355, 1385, 1630 cm^{-1}), it may be assumed that they are due to the quinoinic part of the polymer. Small shifts are observed between some line positions of the HY and HMOR sample. It is suggested that these shifts correspond to the different polymer species in these samples as revealed by their electronic spectra. The Fourier Transform Raman data show clearly the presence of intrazeolite polyaniline.

Infrared spectroscopy allows us to follow the entire sample history from ion exchange to polymerization. The anilinium-loaded zeolite samples show small, but distinct ring vibrations and broad N-H stretch features similar to those of solid aniline hydrochloride, including a diagnostic sharp band at 1495 cm^{-1} (Figure 3). If the anilinium is polymerized in HY zeolite, the typical vibrations of the PANI¹⁴ become dominant as shown by the appearance of bands at 1581, 1500, 1317 and 792 cm^{-1} (Figure 3). In mordenite some residual anilinium indicates that the polymerization was not 100% complete. Lower energy vibrations are obscured by the strong zeolite framework vibrations.

In summary, the combined use of vibrational and electronic spectroscopies proves that intrazeolite anilinium can be polymerized to form polyaniline.

Location of the polyaniline: Intrazeolite or external?

Several observations provide indirect evidence that the polyaniline is stabilized inside the zeolite channel system: The polymerization rate is orders of magnitude slower in the zeolite compared with the bulk reaction - this is explained by the diffusional limitations for the oxidant to reach the anilinium molecules in the channels. No protons are available in solution - therefore, based upon the stoichiometry of the oxidation, the polymerization can only proceed inside the zeolite. Due to the small crystal size of the zeolite host, a detectable fraction of the polymer is expected to be formed at the surface of the crystals.

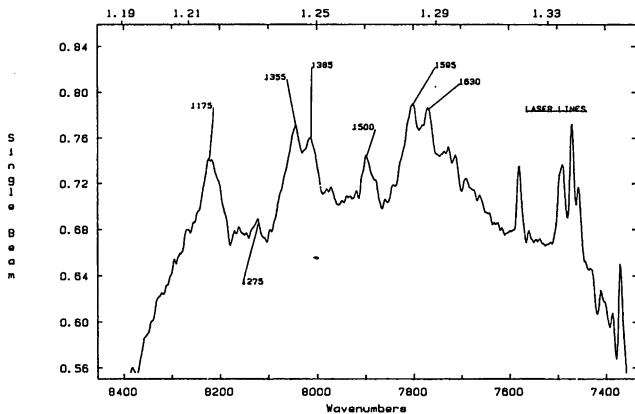


Fig. 2. Fourier Transform Raman spectrum of sample HMOR/P6.

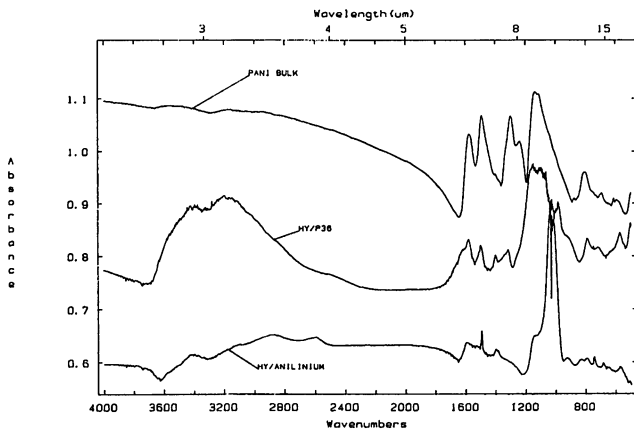


Fig. 3. FTIR spectra of bulk PANI, HY loaded with anilinium, and sample H45Y/P36. Blank zeolite absorbance has been partially subtracted from the zeolite spectra.

This fraction could be successfully removed by extraction with DMSO. Direct evidence for the location of the polymer is obtained from scanning electron micrographs: The zeolite/PANI samples appear exactly as they did before the polymerization, i.e. only a clean crystalline phase is found. No external bulk PANI which would appear as a flaky, amorphous product is observed.

In conclusion, we have succeeded in the controlled synthesis of intrazeolite chains of polyaniline via oxidative polymerization of pre-loaded anilinium ion. Comprehensive spectroscopic characterization elucidates the nature of the polymerization products, while chemical arguments and electron micrographs show that the products are located inside the zeolite channel system. More detailed studies of polyaniline and other polymers in different hosts will be published elsewhere.

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