

Formation of Polypyrrole in Cu^{II} Ion-exchanged MCM-41

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In the last few decades, conductive polymers have been the subject of numerous investigations due to their practical applications such as rechargeable batteries, smart windows, sensors, light emitting diodes (LED) and nonlinear optical devices.¹⁻² Especially, polypyrrole has been regarded as a potential material to be applied in electronic and photo-electrochemical devices because of its high conductivity, environmental stability, redox reactivity and mass production.³ Most of the conductive polymers have conjugation-interrupting defects, such as sp³-hybridized carbons or twists and kinks in polymer chains due to self-aggregation.⁴ Therefore, these structural defects hinder charge transport process in polymers. So, several groups have made efforts to control and modify the physical, structural and electronic properties to solve these structural problems. They have attempted to encapsulate these polymers in heterogeneous hosts, such as zeolites⁵⁻⁹ and layered materials.¹⁰⁻¹³ The heterogeneous hosts could extremely reduce the interchain interaction due to the isolation by the encapsulation. As a result, one could modify their bulk properties.

Bein *et al.* reported a synthetic method for growing various conductive polymers in Y-zeolite.⁵⁻⁸ Roque *et al.* investigated oligomerization of pyrrole by using Fe^{III} ion-exchanged proton-form Y-zeolite.⁹ The presence of oligomers as well as long chain polymers were also proposed in the channels of Cu^{II} ion-exchanged proton-form mordenite through a study on the encapsulation of pyrrole and thiophene.¹⁴⁻¹⁵ However, most of zeolites have heterogeneous micropores with different sizes much less than *ca.* 20 Å. Therefore, it is rather difficult to synthesize homogeneous long polymer chains in zeolites. On the other hand, MCM-41 shows a uniform hexagonal array of linear silica tubes with diameters ranging from 15 to 100 Å and high surface area of about 1000 m²/g.¹⁶⁻¹⁷ Therefore, these properties of MCM-41 have previously been used to isolate the uniform-sized polymer chains.¹⁸⁻¹⁹ This has successful in synthesizing conductive polyaniline by using oxidizing agent.¹⁸

In this work we present the polymerization process of pyrrole in Cu^{II} ion-exchanged MCM-41 without addition of oxidizing agent. Polymerization of pyrrole in MCM-41 channels will give better properties and also overcome the limitation of defects such as self-aggregation. The observed spectroscopic data led us to conclude that the homogeneous

polypyrroles have been synthesized successfully in the cavity of Cu^{II} ion-exchanged MCM-41.

Experimental Section

Materials. Ludox HS-40 colloidal silica (40 wt% suspension in water), Hexadecyltrimethyl ammonium chloride (25 wt% solution in water, HTACl), Ammonium Hydroxide (28% NH₃ in water), Tetrapropylammonium bromide (TPABr), Dodecyltrimethylammonium bromide (DTABr), Aluminium sulfate hydrated, Copper (II) nitrate hemipentahydrate, pyrrole (98%), polypyrrole with dopant were purchased from Aldrich Chemical Co. and used as received. All solvents were obtained from Merck Chemical Co. as spectroscopic grade used without further purification.

AIMCM-41 Synthesis Procedure. AIMCM-41 has been synthesized following a procedure.¹⁶⁻¹⁷ A clear sodium silicate (Na/Si: 0.5) solution was prepared by combining 46.9 g of aqueous NaOH (1.00 M) solution with 14.3 g of a colloidal silica (Ludox HS-40) and heating the resulting gel mixture with stirring for 2 h at 353 K. The sodium silicate solution was dropwise added to a Teflon bottle containing a mixture of 1.2 g of DTABr, 1.04 g of TPABr, 0.29 g aqueous NH₃ solution, 20.0 g of HTACl solution and 10 g deionized water was vigorous magnetically stirred at room temperature. The molar composition of the resulting gel mixture in the bottle was 6 SiO₂ : 1 HTACl : 1.5 Na₂O : 0.15 (NH₄)₂O : 250 H₂O. To prepare the aluminium silicate (Al/Si : 60), 0.53 g of aluminium sulfate hydrate was dissolved deionized water in 5.0 g. After the surfactant and sodium silicate solution was magnetically stirred for 1 h at room temperature, the aluminium sulfate solution was added slowly into the surfactant and sodium silicate solution. After stirring for 2 h more, the gel mixture was heated to 370 K for 1 day. The HTA-silicate mixture was then cooled to room temperature. Subsequently, pH of the reaction mixture was adjusted to 10.2 by dropwise addition of 30 wt% acetic acid with vigorous stirring. The reaction mixture after the pH adjustment to 10.2 and subsequent heating for 1 day was repeated twice more. The precipitated product, AIMCM-41 with HTA template, was filtered, washed with deionized water, and dried in an oven 370 K. The product was calcined in air under static conditions using a tube furnace, and the calcination temperature was increased from room temperature to 823 K over 10 h and maintained at 823 K for 24 h.

Ion Exchange. Ion exchange of the AIMCM-41 was carried out with aqueous Cu (NO₃)₂ · 2.5H₂O (2.1 × 10⁻⁴ M).

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For the ion exchange with Cu^{II} , 1.0 g of the as-calcined AIMCM-41 sample was stirred with 200 mL of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (2.1×10^{-4} M) solution for 12 h at room temperature. After Cu^{II} ion-exchanged was filtered, washed with deionized water, and dried in an oven 370 K. The ion exchange procedure was repeated two times. The ion-exchanged sample was calcined in air under static conditions using a tube furnace, and the calcination temperature was increased from room temperature to 823 K over 10 h and maintained at 823 K for 24 h.

Adsorption and Polymerization of Pyrrole. Monomer adsorption of pyrrole into the Cu^{II} ion-exchanged AIMCM-41 was performed using the following procedure. About 1 g of the Cu^{II} ion-exchanged AIMCM-41 was evacuated in a vacuum reactor under 1.0×10^{-4} Torr while being heated at 373 K for 30 min and 473 K for 2 h. The Cu^{II} ion-exchanged AIMCM-41 was then cooled to room temperature. In a second reactor pyrrole was frozen with liquid nitrogen, evacuated, and thawed again for three cycles. The vacuum reactor in Cu^{II} ion-exchanged AIMCM-41 exposed to pyrrole vapor at room temperature.

Spectroscopic Measurements. X-ray diffractograms were recorded on the MO3X-HF diffractometer (Model-1031, Mac Science Co.). To measure the FT-IR spectra, JASCO FT/IR-410 spectrometer and KBr technique were used. Diffuse reflectance UV-VIS spectra were recorded by using a Shimadzu UV-3101PC spectrometer equipped with an integrating sphere. Absorption spectra of the ground state are evaluated by the Kubelka-Munk function:

$$\frac{K}{S} = \frac{(1-r)^2}{2r} \quad (1)$$

where K and S are absorption and scattering coefficients, respectively, and r is diffuse reflectance. Electron Spin Resonance (ESR) were recorded by using a BRUKER ESP 300E spectrometer at 77 K.

Results and Discussion

The X-ray diffraction (XRD) patterns of the AIMCM-41 and Cu^{II} AIMCM-41 are shown in Figure 1, which have been assigned to a hexagonal array as reported previously,¹⁶⁻¹⁷ indicating that the framework of the synthesized AIMCM-41 is well formed. No change in the XRD patterns was observed when copper(II) is ion-exchanged in AIMCM-41. This indicates that the framework of the AIMCM-41 is not broken after ion-exchange copper(II) as shown in Figure 1.

When pyrrole is added to the Cu^{II} AIMCM-41 samples, the monomer diffuses through the interior of MCM-41 starting the oxidative polymerization. The first evidence of polymerization was a color change as followings. After ion-exchanged with aqueous $\text{Cu}(\text{NO}_3)_2$ solution, the color of the AIMCM-41 turn to light blue. After diffusion of pyrrole, color change from light blue to black was observed, indicating the occurrence of some oxidative polymerization, since the color of bulk polypyrrole prepared by chemical polymerization is black.²⁰

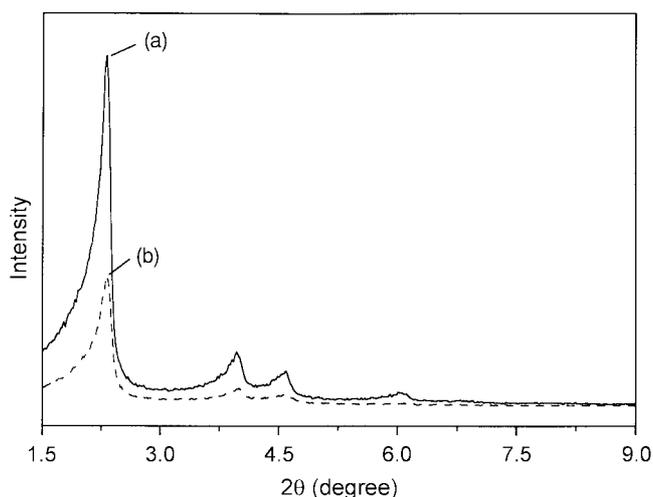


Figure 1. XRD patterns of (a) AIMCM-41 (b) Cu^{II} AIMCM-41.

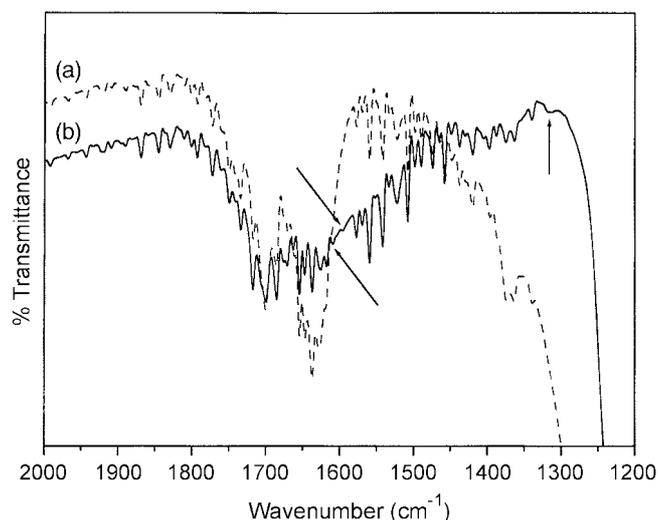


Figure 2. FT-IR spectra of (a) Cu^{II} AIMCM-41 (b) pyrrole/ Cu^{II} AIMCM-41.

Figure 2 shows the FT-IR spectra Cu^{II} AIMCM-41 and pyrrole/ Cu^{II} AIMCM-41. New bands in the spectrum of pyrrole/ Cu^{II} AIMCM-41 were observed at 1315 cm^{-1} , 1595 cm^{-1} and 1610 cm^{-1} compared with that of Cu^{II} AIMCM-41. These additional bands correspond to the characteristic bands of bulk-doped polypyrrole.⁷ However, certain shifts compared with bulk-doped polypyrrole in the IR bands towards higher wavenumbers were observed. These shifts were found to vary with preparation conditions.⁷ Other bands of polypyrrole could not be observed probably due to spectral overlap in Cu^{II} AIMCM-41.

Figure 3 shows the ground state absorption spectra of pyrrole/ Cu^{II} AIMCM-41, as well as bulk-doped polypyrrole. The UV-VIS spectra of pyrrole/ Cu^{II} AIMCM-41 exhibited maxima at 298 nm (*ca.* 4.14 eV), 418 nm (*ca.* 2.96 eV) and 466 nm (*ca.* 2.66 eV). It has been reported that absorption maximum of the monomer is at 211 nm (*ca.* 5.9 eV).²¹ However, we could not observe the monomer absorption

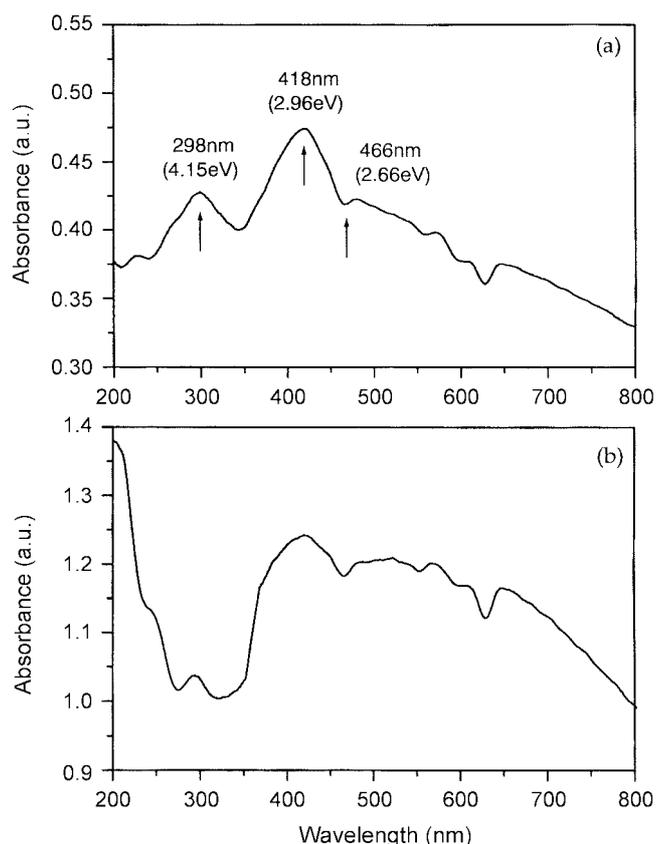


Figure 3. UV-VIS spectra of (a) pyrrole/Cu^{II}AIMCM-41 (b) Bulk-doped polypyrrole.

band in pyrrole/Cu^{II}AIMCM-41. The observed band edge at 466 nm could be assigned to the band gap of neutral polypyrrole formed in Cu^{II} ion-exchanged MCM-41.²⁰ However, we could not observe broad polypyrrole bands, which is usually observed in electrochemical polymerize polypyrrole.³ An appreciable absorbance at lower energy range reveal the co-production of ionic species including polaron. The apparent absorption band at near Infrared region as well as ESR studies on the same samples gives further evidence of the polaron presence in the pyrrole/Cu^{II}AIMCM-41.

The presence of polaron in pyrrole/Cu^{II}AIMCM-41 obtained in this work was confirmed by ESR spectroscopy. The ESR spectrum of pyrrole/Cu^{II}AIMCM-41 is shown in Figure 4. The spectrum shows a signal at about $g = 1.99$.²²⁻²⁴ Such a sharp symmetrical ESR signal, of which g value is close to that of free electron is typical in organic radicals or polaron species formed in conductive polymers. The ESR spectrum of pyrrole/Cu^{II}AIMCM-41 did not show evidence of the Cu^{II} presence.²² These results indicated most of Cu^{II} ions are reduced to Cu^I ions by oxidizing of nitrogen in pyrrole ring. The radical cations combine in a series of steps to yield polypyrrole. Finally, homogeneous polypyrrole could be obtained in pyrrole/Cu^{II}AIMCM-41 system.

Based on the above spectroscopic data we have demonstrated that polypyrrole is formed in Cu^{II} ion-exchanged MCM-41 channels. It was found that Cu^{II} ion of the mesoporous silicate framework acts as a good oxidizing

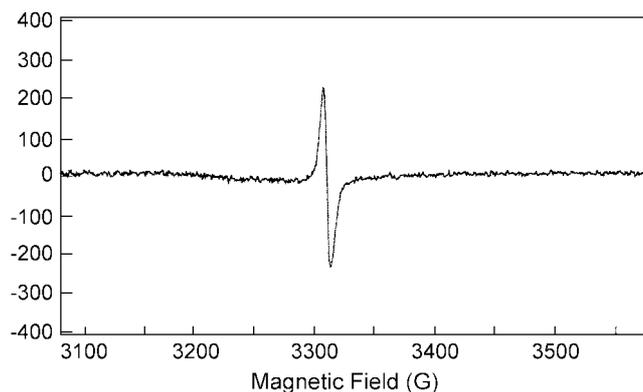


Figure 4. ESR Spectrum of polypyrrole radicals in Cu^{II} AIMCM-41.

agent for polymerization reaction. The advantage of this method is that the procedure is simple, because it does not require another initiator during polymerization. From the spectroscopic data of pyrrole/Cu^{II}AIMCM-41 we conclude very long polymer chains successfully formed in pyrrole/Cu^{II}AIMCM-41. Therefore, the Cu^{II} ion-exchanged MCM-41 channels would be very useful as heterogeneous hosts for long polymer chains.

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