

IN SITU SPONTANEOUS POLYMERIZATION OF PYRROLE IN CUPRIC ION EXCHANGED MONTMORILLONITE

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The spontaneous polymerization of pyrrolium ions within the confined environment of montmorillonite (MMT) is described. In this study, previously purified montmorillonite (Na^+ -MMT) is ion-changed with Cu(II) and cupric ion-exchanged montmorillonite [Cu(II)- MMT] is first prepared. The Cu(II)-MMT is then characterized by the techniques described below. The Cu(II)-MMT sample is then treated with 0.1 M pyrrole in 0.1 M HCl(aq) solution. This has resulted in the intercalation of pyrrolium ions within the interlayer regions of Cu(II)- MMT host followed by one-step spontaneous polymerization to result in Cu(I)-PPY-MMT nanocomposite material (PPY stands for polypyrrole). The as-synthesized nanocomposite material has been characterized by FTIR (Fourier Transformed InfraRed) spectroscopy, X-ray diffraction (XRD) and four point probe method. The ionic and electronic conductivity of Cu(I)-PPY-MMT are higher than those of other MMT-polypyrrole materials prepared previously in our laboratory. Interestingly, pyrrolium ions are polymerized spontaneously within the confined environment of Cu(II)-MMT but the same does not take place in the aqueous solution containing Cu(II) ions. This suggests that the microstructure of Cu(II) coordinated to MMT plays an important role in changing the thermodynamic properties of Cu(II)-Cu(I)-Cu(0) redox systems. Further the instability of Cu(I) in water due to its fast disproportionation may lead to the inability of Cu(II) to polymerize pyrrole in water. However, in the confined environment, the coordinated Cu(I) in the solid form is thermodynamically stable and the electrode potential of Cu(II)-Cu(I) system is sufficient for the oxidative polymerization of pyrrole. We, therefore, propose that initial exchange of some Cu(II) ions for pyrrolium ions leads to the initial intercalation of pyrrolium ions into the interlayer spaces of MMT. This has been confirmed by the presence of Cu(II) in the supernatant of Cu(II)-MMT that has been treated with pyrrolium ions. The polymerization of pyrrolium ions reduces Cu(II) to Cu(I) and the latter present in the polypyrrole matrix contributes to the enhanced ionic conductivity. The higher uptake of polypyrrole is shown by the greater increase in d-spacing measured in the XRD. This system gives a d-value of 16 Å due to polypyrrole and this value does not change with heat-treatment suggesting that it is an inherent d-value due to polypyrrole. The polypyrrole matrix which is now coordinated to Cu(I) ions expels coordinated water in the metal ions. The polypyrrole-Cu(I) present within the interlayers of MMT has a favorable path for Cu(I) ions to move about by hopping through coordinated sites which gives rise to a fast ion-conducting properties for the nanocomposite.

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