A NOVEL METHOD OF ALUMINA FUNCTIONALISATION BY SILYLATION AND COVALENT GRAFTING OF POLYANILINE

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ABSTRACT

Alumina is widely used in a variety of processes including removal of impurities and catalyst preparation[1]. The hydroxyl groups on the alumina surface can be utilised for functionalisation with organic compounds. In the present study, an alumina-polyaniline (PANI) hybrid has been prepared by applying a “low-solvent” method of silylation using a very small amount of methanol as solvent, followed by grafting of PANI[2]. Further improvement from the previously developed method has been achieved by eliminating dedoping as an additional operation to separate free PANI homopolymer from the hybrid product.

The alumina used in the experiments was “Aluminium oxide 90 Standardized” (Merck), which was thermally pre-treated in vacuum at 120°C for 24 h. The coupling agent, 3-(phenylaminopropyl)trimethoxysilane (PAPTMOS) was dissolved in a small amount of absolute methanol. Thus, for 1 g of alumina 0.25 g of PAPTMOS was dissolved in 1 ml of methanol. The reaction mixture was heated at 110°C in vacuum for about 40 h. The long heating time was used to ensure complete reaction. The product was washed with methanol or methanol and acetone by centrifugation, isolated, and vacuum dried at 60°C for 24 h. Diagnostic FTIR bands at 1602 and 1506 cm^{-1} for the benzene ring confirmed the presence of silane coupling agent in the product, and the C:N ratio obtained from elemental analysis showed about 12% PAPTMOS bonded to alumina.

Grafting of PANI was carried out by suspending the silylated reaction product in a solution of aniline in 1 M aqueous HCl or methanesulfonic acid (MSA), and adding aqueous ammonium peroxydisulfate dropwise with constant stirring. The dark green product was washed with water and dedoped by treatment with aqueous ammonia overnight, then washed with tetrahydrofuran and 1-methyl-2-pyrrolidone (NMP) to remove physically adsorbed PANI homopolymer. The C:N ratio obtained from elemental analysis was about 6, which indicates the presence of PANI in the above product. Strong signals at 1597 and 1508 cm^{-1}, characteristic of the benzyl radicals of non-conductive PANI emeraldine base, were observed from FTIR studies.

The improvement was done when the ammonia dedoping stage was omitted, by treating the reaction product (a mixture of PANI-grafted to silylated alumina and PANI homopolymer) with a binary system of solvents, containing NMP and an amine, specifically triethylamine (TEA), or diethylamine (DEA), or ethylenediamine (EDA), with volume ratios NMP:TEA, 30:3; NMP:DEA, 30:2.5; NMP:EDA, 30:1.5. This treatment converts doped PANI to its dedoped form, via acid-base reaction with the strong aliphatic bases, and thus solubilises the PANI homopolymer and thereby removes it from the reaction mixture in a single step.

The PANI-grafted alumina formed by each procedure was re-doped with 1 M aqueous MSA to obtain the green emeraldine salt (conductive form) of PANI, washed with water and acetone, then vacuum dried at 50^{o}C. The conductivity of the PANI grafted alumina was 8×10^{-5} S cm^{-1} (4-point probe method). The products of all the stages were further characterised by X-ray photoelectron spectroscopy, solid state ^{29}Si and ^{13}C NMR spectroscopy, and scanning electron microscopy.

References:

(1) Demirbas, A. *Energy Sources, Part A* **2009**, *31*, 671–678.
(2) Wheelwright, W. V. K.; Ray, S.; Easteal, A. J. *Macromolecular Symposia* **2010** *(in press)*.