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ORIGINAL PAPER

Synthesis of novel fluorene-functionalised nanoporous silica and its luminescence behaviour in acidic media

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Fluorene-functionalised nanoporous silica (FL-NH_2-SBA-15) was prepared using the post-synthesis grafting method of SBA-15. The material thus obtained was characterised by means of small- and wide-angle X-ray diffraction, nitrogen adsorption–desorption, Fourier transform infrared spectroscopy, Raman spectroscopy, thermogravimetric analysis, and elemental analysis. The results showed that the organised structure is preserved after the post-grafting procedure. Surface area and pore-size decreased by attaching functional groups to the pore surface. In addition, the pore volume was reduced with functionalisation. The amount of fluorene grafted onto the surface of SBA-15 was 0.55 mmol with a yield of approximately 46 %. The emission spectra of FL-NH_2-SBA-15 in acidic media were studied and are discussed in detail. The structural change between FL-NH_2-SBA-15 and the protonated form might be an effective candidate for acid-dependent molecular-sensor models for advanced application in molecular sensors in the future.

Keywords: nanoporous silica, SBA-15, post synthesis, fluorene, fluorescence

Introduction

Out of the nanoporous silica materials, SBA-15 is the one with the large pore-size and high surface area, flexible surface chemistry to functionalisation, and well-defined ordered structure found in siliceous nanostructured materials (Bagshaw et al., 1995; Beck et al., 1992; Kresge et al., 1992; Taguchi & Schüth, 2005; Tanev & Pinnavaia, 1995; Zhao et al., 1998a). The siliceous wall surface can be modified with organic groups to alter their properties and achieve specific purposes (Badiei et al., 2011; Khaniani et al., 2012; Stein et al., 2000). Functionalisation of these materials can be carried out by grafting onto the surface of the preformed silica via a silanol group which reacts with an organoalkoxysilane compound supporting the active functional group. Post-synthesis grafting by adding an organosilane to the synthesis mixture is one of the popular strategies for the immobilisation of functional groups onto mesoporous silica via covalent bonds (Stein et al., 2000; Vinu et al., 2005; Zhao et al., 1998a).

Fluorene is a polycyclic aromatic hydrocarbon and has been known for seventy years. Fluorene as a kind of rigid plane constitutes a pair of phenyl rings linked with a five-member ring providing a high overlap of π-orbital (Belfield et al., 2004). It has high luminescent efficiency and high flexibility to modify the molecular skeleton. In this regard, fluorene-based blue-emitting materials are widely used in the synthesis of host materials, white light-emitting materials, organic lasers, and organic nanomaterials (Belfield et al., 2004; Fitilis et al., 2007). Fluorene derivatives are used in applications of thermo and light sensitisers and organometallic-complexes. Zheng et al. (2007) reported on absorption and fluorescence pH sensors based on 9-(cycloheptatrienylidene)fluorene (9-CHF) derivatives. These compounds are used not only as an absorption sensor in strong acidic media (1.5 mol L^{-1} to 3.5 mol L^{-1} H_2SO_4 in ethanol); they act as fluo-

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