Abstract

Self-assembled multidoped cryptomelane hollow microspheres with ultrafine particles in the size range of 4–6 nm, and with a very high surface area of 380 $m^2\ g^{-1}$ have been synthesized. The particle size, morphology, and the surface area of these materials are readily controlled via multiple framework substitutions. The X-ray diffraction and transmission electron microscopy (TEM) results indicate that the as-synthesized multidoped OMS-2 materials are pristine and crystalline, with no segregated metal oxide impurities. These results are corroborated by infrared (IR) and Raman spectroscopy data, which show no segregated amorphous and/or crystalline metal impurities. The field-emission scanning electron microscopy (FESEM) studies confirm the homogeneous morphology consisting of microspheres that are hollow and constructed by the self-assembly of pseudo-flakes, whereas energy-dispersive X-ray (EDX) analyses imply that all four metal cations are incorporated into the OMS-2 structure. On the other hand, thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) demonstrate that the as-synthesized multidoped OMS-2 hollow microspheres are more thermally unstable than their single-doped and undoped counterparts. However, the in-situ XRD studies show that the cryptomelane phase of the multidoped OMS-2 hollow microspheres is stable up to about 450°C in air. The catalytic activity of these microspheres towards the oxidation of diphenylmethanol is excellent compared to that of undoped OMS-2 materials.