

Abstract

Cobalt-doped cryptomelane-type manganese oxide (K-OMS-2) microwires have been successfully synthesized and characterized. Their catalytic activity was tested in an oxidation reaction with benzyl alcohol as the substrate, and the cobalt-doped OMS-2 materials showed 100% selectivity toward benzyl aldehyde with a conversion of 55%. The cobalt-doped OMS-2 materials were also investigated as a desulfurization sorbent in a fixed bed reactor at 250 °C where high sulfur sorption capacities (49.4 g of sulfur/100 g of sorbent) were observed. Here, structure-controlled synthesis was performed using a facile one-step microwave-assisted hydrothermal method (MWHY) associated with a rapid temperature ramping (200 °C/min). The structural effects induced by the compositional control of transition metal dopants on the cryptomelane (space group $I4/m$) body centered tetragonal structure were identified with X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD and TEM results showed that the systematic variance of the cobalt content was accompanied by a stepwise lattice expansion of the (110) plane from 6.70 to 7.43 Å. The XRD, high resolution TEM (HRTEM)/TEM, Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) data suggested that the as-synthesized cobalt-doped OMS-2 materials were also crystalline with no segregated metal oxide impurities. The uniform morphology of the metal-doped OMS-2 materials was observed by the field-emission scanning electron microscopy (FESEM), whereas energy-dispersive X-ray (EDX) analysis confirmed the successful incorporation of metal dopant into the OMS-2 structure. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed a higher degree of doping ($\text{Co/Mn} = \sim 0.26$) associated with the MWHY method over conventional methods. On the other hand, TGA demonstrated that the as-synthesized materials were more thermally unstable than their undoped counterparts. The observed structural and chemical characteristics upon doping with some metal cations were explained by the Jahn–Teller distortion.