Raquel P. Rocha, Olívia Salomé G.P. Soares, José J.M. Órfão, Manuel F. R. Pereira, J.L. Figueiredo

Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM)
Faculty of Engineering, University of Porto,
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

rprocha@fe.up.pt

Novel solvent-free method for the synthesis of cryptomelane-type manganese oxide nanorods

Development of novel oxides for the replacement of critical catalysts, such as noble metals, is attracting a great deal of attention. Co, Cu, Ni and Mn oxides are being widely studied due to their lower cost and higher resistance to deactivation, in comparison to supported noble metals. Among the manganese oxides, cryptomelane is considered a very interesting material, due to its open tunnel structure, mixed valence of manganese and high mobility of lattice oxygen [1]. The development of fast, simple and low cost preparation methods of highly active oxides is still a challenge, especially for their large scale production. Therefore, the aim of this work was the preparation of stable and efficient manganese oxide catalysts as an alternative to traditional noble metals, and their evaluation in the catalytic oxidation of volatile organic compounds (VOC), which is a promising technology for cleaning contaminated gaseous emissions.

Novel solvent-free reaction and reflux approach methods were used to synthesize cryptomelane-type materials. These oxides, and others produced by conventional methods, were tested as catalysts for the oxidation of ethyl acetate and butyl acetate, which are representative of volatile organic compounds found in industrial emissions. The prepared nanomaterials were characterized by several techniques such as: N_2 adsorption at -196 °C, XRD, SEM, TPR and XPS.

The materials synthesized by the solid-state reaction method and by the reflux approach lead to the formation of cryptomelane phases presenting a homogeneous nanorod morphology, with diameters between 10-20 nm using the solvent free method (Figure 1), and nanorods with 30 nm when using the reflux approach. Conventional methods lead to a mixture of manganese oxide phases (Mn_3O_4, Mn_5O_8 and α–Mn_2O_3) with lower reactivity and distinct morphologies. All the manganese oxides proved to be very active for the oxidation of ethyl acetate and butyl acetate into carbon dioxide, the samples with cryptomelane nanorods synthesized by the new solvent-free method being more active than those prepared by the conventional methods.

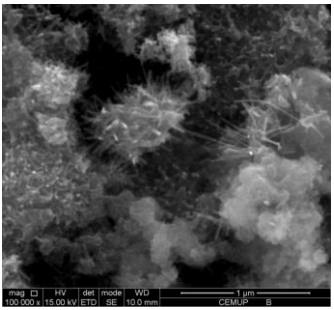

Figure 1: SEM micrograph of the novel cryptomelane nanorods prepared by solid-state reaction.

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