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Comparison of the Thermal Behavior of Different Crystal Forms of Manganese(II) Oxalate

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Abstract : Sparingly soluble manganese oxalate is an appropriate precursor for the preparation of nanosized manganese oxides, which have a wide range of technological application. During the precipitation of manganese oxalate, three crystal forms could be obtained – α-$MnC_2O_4.2H_2O$ (SG C2/c), γ-$MnC_2O_4.2H_2O$ (SG P212121) and orthorhombic $MnC_2O_4.3H_2O$ (SG Pcca). The thermolysis of α-$MnC_2O_4.2H_2O$ has been extensively studied during the years, while the literature data for the other two forms has been quite scarce. The aim of the present communication is to highlight the influence of the initial crystal structure on the decomposition mechanism of these three forms, their magnetic properties, the structure of the anhydrous oxalates, as well as the nature of the obtained oxides. For the characterization of the samples XRD, SEM, DTA, TG, DSC, nitrogen adsorption, and in situ magnetic measurements were used. The dehydration proceeds in one step with α-$MnC_2O_4.2H2O$ and γ-$MnC_2O_4.2H_2O$, and in three steps with $MnC_2O_4.3H2O$. The values of dehydration enthalpy are 97, 149 and 132 kJ/mol, respectively, and the last two were reported for the first time, best to our knowledge. The magnetic measurements show that at room temperature all samples are antiferomagnetic, however during the dehydration of α-$MnC_2O_4.2H_2O$ the exchange interaction is preserved, for $MnC_2O_4.3H_2O$ it changes to ferromagnetic above 35°C, and for γ-$MnC_2O_4.2H_2O$ it changes twice from antiferomagnetic to ferromagnetic above 70°C. The experimental results for magnetic properties are in accordance with the computational results obtained with Wien2k code. The difference in the initial crystal structure of the forms used determines different changes in the specific surface area during dehydration and different extent of Mn(II) oxidation during decomposition in the air; both being highest at α-$MnC_2O_4.2H_2O$. The isothermal decomposition of the different oxalate forms shows that the type and physicochemical properties of the oxides, obtained at the same annealing temperature depend on the precursor used. Based on the results from the non-isothermal and isothermal experiments, and from different methods used for characterization of the sample, a comparison of the nature, mechanism and peculiarities of the thermolysis of the different crystal forms of manganese oxalate was made, which clearly reveals the influence of the initial crystal structure.
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