Application of mass spectral analysis to the studying of decomposition mechanism of some oxalate specimens

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During the last years the interest in the utilization of 3d-transition metal oxalates of the so-called "magnesium series" (Mg, Mn, Fe, Co, Ni, Zn) as precursors for nanosized oxide materials and metal powder has been growing considerably. In this application the good knowledge of the mechanism of oxalate decomposition is very important. A specific feature of these systems is the liberation of CO_2, as well as CO, which is capable of reducing the obtained oxide. This way the oxide with a lower oxidation state of M^{n+} could be formed and even a metal phase could appear (at Ni, Co, Cu oxalates). The Evolved gas analysis with following mass spectrometry (EGA-MS) of the liberated H_2O, CO and CO_2 is very appropriate for tracing the oxalate decomposition mechanism. The proceeding of the examination in vacuum eliminates the possibility for any secondary oxidizing processes occurring in air medium and thus disguising the true mechanism.

The objects investigated are $CoC_2O_4.2H_2O$, $Ni_{0.34}Mn_{0.66}C_2O_4.2H_2O$ and $Ni_{0.11}Mn_{0.89}C_2O_4.2H_2O$. They were characterized by XRD and SEM analyses. The mass-spectral studies were carried out applying linear temperature program and this way the kinetic curve of the process was obtained.

For $Ni_{0.34}Mn_{0.66}C_2O_4.2H_2O$ and $Ni_{0.11}Mn_{0.89}C_2O_4.2H_2O$ system it was established that the Ni content influenced on the morphology of the sample, temperature of dehydration and decomposition, and on the amount of liberated CO. The decreasing in the CO amount upon increasing the Ni content suggests the reduction of Ni^{2+} in vacuum from liberated CO in accordance with Ellingham diagrams.

The EGA-MS examinations of $CoC_2O_4.2H_2O$ show that the dehydration process is uncompleted and overlaps with the oxalate decomposition. The dn/dT curves reveal almost equal amounts of CO and CO_2 released, but the CO-evolution proceeds somewhat faster than that of CO_2.