

PREPARATION OF MIXED-OXIDE MATERIALS FROM HETEROMETALLIC COORDINATION COMPOUNDS

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The increasing demand for heterometallic oxides is associated with the broad spectrum of their valuable properties. The performance of many oxide materials is extremely sensitive to the synthesis conditions [1, 2]. A convenient way of getting mixed-oxides is the single source molecular precursor (SSMP) method [3]. Ideally, a SSMP contains the required metal atoms in the ratio that corresponds to the stoichiometry of the desired multimetallic oxide. However, the synthesis of heterometallic compounds, which can act as SSMPs, represents an ambitious challenge because of the frequently divergent electronic and coordination requirements of the different metals.

Aminopolycarboxylate (APC) complexes are promising SSMP candidates due to a wide variety of available ligands with high coordination capacity and variable charge which afford an easy adjustable stoichiometry of the target metals. Moreover, the composition of the precursors can be readily adjusted by using appropriate aminopolycarboxylates or additional ligands to achieve an optimal amount of combustible material.

Along this line, we have started a systematic investigation of the influence of APC ligands, of the intermetallic distances, of the combustible material, of the heating rate and of the working atmosphere on the thermal degradation processes of heterometallic precursors and on the composition and microstructure of the final residue. For this purpose, two series of heterometallic complexes of general formula $Ba\{M(APC)\}X \cdot nH_2O$ ($M = Co^{2+(3+)}$, Mn^{2+} ; $X =$ no specie, H^+ or CH_3COO^-) and $M(L)_y\{Bi(APC)\}_z \cdot nH_2O$ ($M = VO^{2+}$, Cu^{2+} , Cr^{3+} ; $L = 2,2'$ -bipyridine or urea; $y = 0, 1, 2$ or 6 ; $z = 1$ or 2 ; $n = 5 - 16$) have been synthesized and probed as SSMPs for the preparation of Ba-Co(Mn)-O or Bi-V(Cu,Cr)-O mixed-oxides. As APC ligands we have successfully used nitrilotriacetate (nta^{3-}), ethylenediaminetetraacetate ($edta^{4-}$), 1,2-cyclohexanediaminetetraacetate ($cdta^{4-}$) or diethylenetriaminepentaacetate ($dtpa^{5-}$).

It was found that the cumulative effect of short intermetallic separations and appropriate amount of combustible material from the precursors combined with heating in flowing air or oxygen at low rates can produce pure heterometallic oxides. The conditions required to prepare the oxide materials from SSMP are significantly milder than what has been previously reported for other methods. The differences observed in the grain size and morphology between the considered residues demonstrated that the nature of the initial organic ligands and heating rate can affect the microstructural properties of the final bimetallic oxides.

References:

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