Oxoalkoxides—True Precursors of Complex Oxides

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Abstract. X-ray structural analysis of “crystalline alkoxides” in many cases reveals that along with OR-groups their molecules also contain oxo-ligands. The following possible reactions leading to formation of oxoalkoxides have been discussed: hydrolysis, pyrolysis (frequently uncontrollable), ether elimination, oxidation of OR-groups (which exist in solutions of alkali, alkaline-earth and rare earth elements), or alkoxides of the lower oxidation states (which are formed by reduction of M(OR), on cathode during electrolysis or by hydrogen in statu nascendi). Oligomeric oxoalkoxides differ from the polymeric alkoxides M(OR), in considerably higher solubility and reactivity. The most important role of oxoalkoxides in the processes of formation of oxides has been demonstrated using as an example preparation of BaTiO3 from alkoxides.

Keywords: metal alkoxides, oxoalkoxides, precursors chemistry, barium titanate

1. Introduction

The present review represents the results of the studies in the field of chemistry of alkoxides and their applications for preparation of oxides which have been obtained in the Moscow State University and L.Va. Karpov Institute of Physical Chemistry [1]. The results of these long-standing works give a scientific base for the development of sol-gel technology of alkoxides and alkoxy-derived powders during the last few years in Russia in NIPIM (Tula). The direct electrochemical synthesis of alkoxides from metals provides a means for the commercial production of alkoxides for sol-gel technology [2]. In the course of the study of sol-gel processes the main attention has been paid to synthesis of complex oxide materials—titanates, zirconates, niobates, tantalates, tungstates, molybdates of alkali alkaline-earth metals (in the form of powders and thin films). Ferroelectrics, high temperature superconductors, solid electrolytes are among the studied complex oxides [3, 4].

Interaction in solutions of two alkoxides were studied by construction of solubility diagrams for the tri-component systems M(OR),-M(OR),-L where M = M(I), M(II), Sc, Y, Ln, Al, Bi; M' = Al, Ti, Zr, Nb, Ta, Mo, W; R = ROH, C6H6, THF; about 50 diagrams have been studied [5].

2. Structures of Oligomeric Oxoalkoxides

The most essential results in the chemistry of alkoxides recently involve structural data. In the case of study and identification of mono- and bimetallic oxoalkoxides direct structural investigations are required. In many cases it is impossible to distinguish between alkoxides and oxoalkoxides without X-ray structural analysis of single crystals. Chemical analysis in most cases is useless because oxoalkoxides are often solvated by alcohols.

One of the first sensational results were obtained when the structures of Y, Sc, In, Ln “isopropoxides” were solved by Bradley and coworkers [6] and Caulton and Hubert-Pfalzgraf [7]. These molecules turned out to the oxoalkoxides with the central oxygen atom surrounded by five metal atoms—M5(μ5-O)(OPr-i)13. The most important role of oxoalkoxides in the processes of formation of oxides has been demonstrated using as an example preparation of BaTiO3 from alkoxides.
Fig. 1. Molecular structure of oxoalkoxides. (a) "Al(OEt)\textsubscript{3}\textsuperscript{3−} = \text{Al}_{10}(\mu_4-O)_2(\mu_3-O)_2(OEt)_{22}; (b) "Ca(OEt)\textsubscript{2} 2EtOH" = \text{Ca}_6(\mu_4-O)_2(\mu_3-OEt)_4(OEt)_{14}EtOH; (c) "Pb(OH)(OR)" = \text{Pb}_6(\mu_3-O)_4(\mu_3-OPr-i)_4."