

METAL ALKOXIDES AND DIKETONATES

Metal alkoxides are compounds in which a metal is bonded to one or more alkyl groups through an intermediate oxygen atom. Metal alkoxides can be considered derivatives of alcohols in which a hydroxyl hydrogen is replaced by a metal. Metal alkoxides are frequently associated by intermolecular forces into tight complexes. *Double metal alkoxides* are complexes of metal alkoxides containing two different metal atoms. *Metal diketonates*, most commonly metal pentanedionates, are related compounds in which a metal atom has replaced an enolic hydroxyl hydrogen of a diketone and is bound or coordinated to one or two oxygens of the resultant diketonate anion. Many metal diketonates have structures where the coordination number of the metal exceeds the valence number.

Physical Properties

Metal alkoxides exhibit great differences in physical properties depending primarily on the metal and secondarily on the alkyl group. Many metal alkoxides are strongly associated by intermolecular forces which depend on the size and shape of alkyl groups. The degree of association of metal alkoxides can be described by the term molecular complexity, the average number of empirical units in a complex. Metal diketonates, similarly, can be dimeric, trimeric, tetrameric, etc. Metal diketonates of alkali metals, however, are "salt-like" in their physical properties and highly dissociated in ethanol.

The fact that many metal methoxides are solid non-distillable compounds can be explained by the small screening effect on the metal atom by the methyl group. With a larger number of methyl groups and smaller atomic radius of the metal, methoxides become sublimeable or even distillable. Branching of the alkyl group, i.e. t-butyl vs. n-butyl usually enhances volatility and decreases molecular complexity. Titanium alkoxides provide a good example of this trend.

Many metal alkoxides are soluble in corresponding alcohols. Only distillable alkoxides are soluble in non-polar solvents.

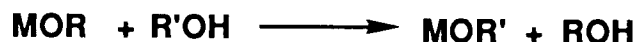
Metal alkoxides are colored when the corresponding metal ion is colored.

Chemical Properties

The most conspicuous property of metal alkoxides is ease of hydrolysis. In general, speed of hydrolysis is proportional to the electropositive character of the element or its' ability to enter a hyper-coordinate state. In contrast, most metal diketonates resist hydrolysis or hydrolyze only slowly.

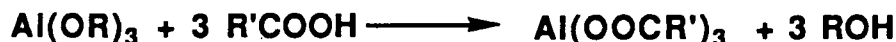


Metal alkoxides exchange alcohols in equilibration reactions similar to transesterification.

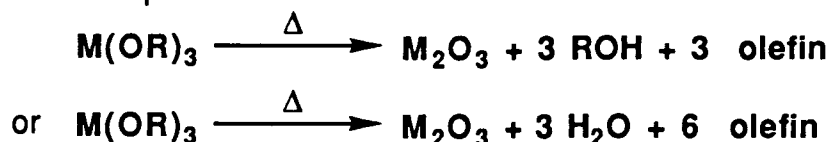


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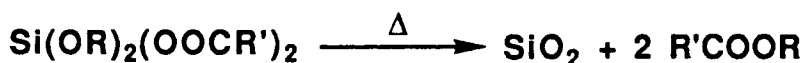
Metal alkoxides react with carboxylic acids to give metal salts.



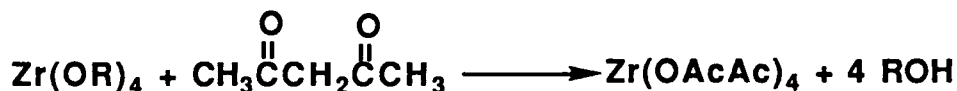
Many metal alkoxides are employed in Chemical Vapor Deposition (CVD) processes for refractory and dielectric oxides. Pyrolysis is generally assumed to proceed through one of two sequences.



Mixed metal alkoxide carboxylates are frequently unstable, yielding metal oxides and carboxylic esters upon thermal degradation. Physical mixtures of metal alkoxides and metal carboxylates may degrade thermally to give similar products.

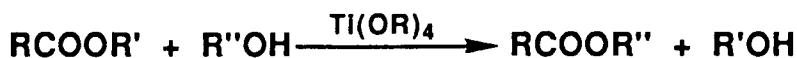


Enols can react with metal alkoxides to give chelates with the elimination of alcohol.

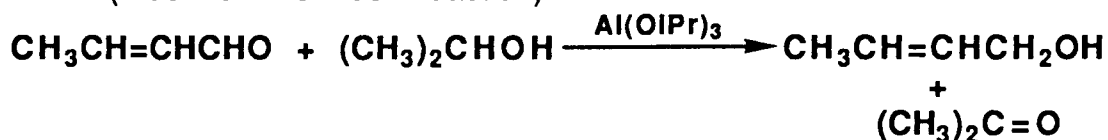


Metal alkoxides are active catalysts for a number of reactions including:

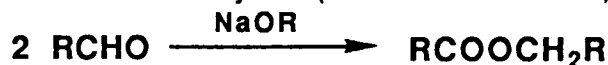
1) the transesterification of carboxylic esters



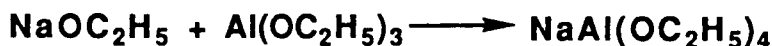
2) the cross oxidation-reduction of ketones and secondary alcohols (Meerwein-Ponndorf reaction).



3) the condensation of aldehydes (Tischenko reaction).



Some metal alkoxides can react with each other to form double metal alkoxides.



SOL-GEL APPLICATIONS OF METAL ALKOXIDES

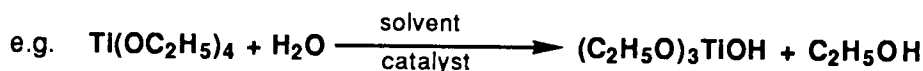
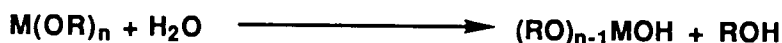
Sol-Gel is a method for preparing specialty metal oxide glasses and ceramics by hydrolyzing a chemical precursor or mixture of chemical precursors that pass sequentially through a solution state and a gel state before being dehydrated to a glass or ceramic.

Sol-gel technology has expanded dramatically since 1980 with the development of a variety of techniques to prepare fibers, microspheres, thin films, fine powders and monoliths. Applications for sol-gel technology include protective coatings, catalysts, piezoelectric devices, wave-guides, lenses, high strength ceramics, superconductors, insulating materials and nuclear waste encapsulation. The flexibility of sol-gel technology allows unique access to multi-component oxide systems and low temperature process regimens.

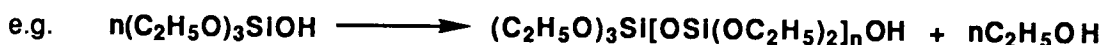
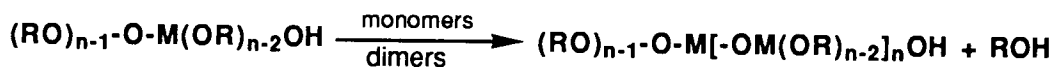
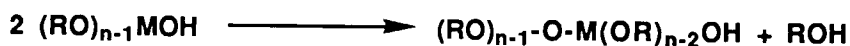
Process Technology and Chemistry

Preparation of metal oxides by the sol-gel route proceeds through three basic steps: 1) partial hydrolysis of metal alkoxides to form reactive monomers; 2) the polycondensation of these monomers to form colloid-like oligomers (sol formation); 3) additional hydrolysis to promote polymerization and cross-linking leading to a 3-dimensional matrix (gel formation). Although presented sequentially, these reactions occur simultaneously after the initial processing stage.

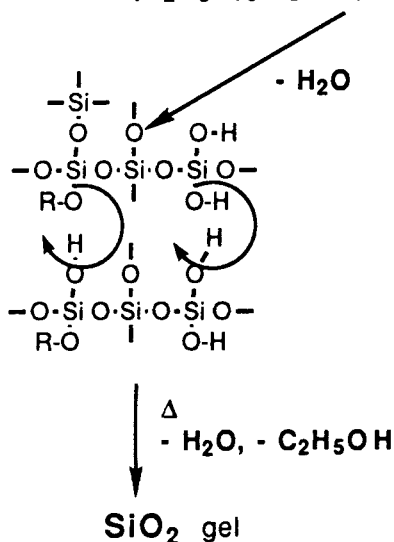
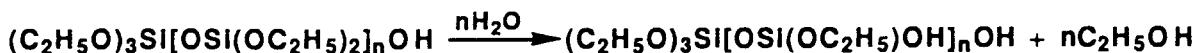
MONOMER FORMATION (PARTIAL HYDROLYSIS)



SOL FORMATION (POLYCONDENSATION)



GELATION (CROSS-LINKING)



As polymerization and cross-linking progress, the viscosity of the sol gradually increases until the sol-gel transition point is reached. At this point the viscosity abruptly increases and gelation occurs. Further increases in cross-linking are promoted by drying and other dehydration methods. Maximum density is achieved in a process called densification in which the isolated gel is heated above its glass transition temperature. The densification rate and transition (sintering) temperature are influenced primarily by the morphology and composition of the gel.

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