



CHAPTER I INTRODUCTION

Oxide materials are currently prepared via solid state reactions between oxide powders. These reactions are performed at high temperature leading to the stable dense thermodynamic phases. However, many research activities have been aimed at the development of the soft chemistry approaches to the synthesis of inorganic oxides. The most important process amongst these has been the sol-gel process; in its most common form, it involves the hydrolysis and condensation of inorganic precursors to produce a gel which can be converted into an inorganic oxide.¹⁻² In addition, mixed-metal oxide systems that can be also produced via the sol-gel method are of particular interest because an opportunity exists for generating materials intermixed at the atomic level.³⁻⁶

The sol-gel process is one of the most promising ways to append various functionalities to ceramic materials. Sol-gel chemistry is performed at room temperature and is based on polymerization reactions. Starting from molecular precursors, metal alkoxides or inorganic salts, a macromolecular oxide network is obtained via hydrolysis-condensation reactions.⁷⁻¹⁰

Sol-gel processing with the use of alkoxides as precursors has gained a significant level of interest in the past years for the production of advanced materials. Important advantages of this method are that it allows careful control of the size and morphology of cluster/particles in the sol or gel during the early-stage processes, so that high-quality end products can be developed which can fulfil specific demands. It is also possible to design materials of specific macroscopic morphology, such as in ultra-fine particles, fibres, thin films, and monolith. In addition, this method eliminates some impurities commonly found in those processes with inorganic salts in aqueous solvents.¹¹⁻¹²

Metal alkoxides are popular metal-oxide ceramic precursors because of the purity of the starting materials, the low temperature at which the reactions occur, and the ease of the reactions. Simple metal alkoxides $M(OR)_n$ with usual OR ligands are commercially available for a large number of metals. However, there are some

significant drawbacks of simple metal alkoxides which make it difficult to investigate their structures. These are their relatively high cost, low hydrolytic stability, and high reactivity towards water.¹³⁻¹⁴ The high reactivity is the main problem in processing inorganic oxides from alkoxides by the sol-gel method. Many studies have attempted to solve these problems by modifying the simple alkoxide precursors to reduce hydrolytic reactivity in order to avoid a precipitate formation.¹⁵⁻¹⁷ The general approach is to replace one or more alkoxide ligands by groups which are less easily hydrolyzed and additionally block coordination sites at the metal. However, the modifications are rather complicated and expensive. The synthesis of new metal alkoxides possessing unique structures and properties is therefore important for the study of sol-gel processes and the evolution of the metal alkoxide chemistry.

Anodic dissolution of the metal can provide an easy and straightforward way to scale up synthesis of alkoxides for many metals.¹⁸ Reactions between oxides or hydroxides and dialkylcarbonates, polyols or aminoalcohols can also be costly effective routes to new metal alkoxides of some elements.¹⁹⁻²⁰ This route is termed as the 'oxide one-pot synthesis' (OOPS) process. Interestingly, metal derivatives of glycol²¹⁻²⁹ or aminoalcohol³⁰⁻³³ are comparatively more hydrolytic resistant than their alkoxide analogues. The chelating nature of the glycol/aminoalcohol and coordinative saturation achieved by the central atoms in the final products appear to be the main factor for their hydrolytic stability to retard the hydrolysis and condensation reaction rates in order to obtain homogeneous gels rather than precipitates.¹⁷

1.1 Porous Oxide Materials

Porous materials created by nature or by synthetic design have found great utility in all aspects of human activity. Porous ceramics have been employed in a great number of industrial areas, particularly in ceramic catalysts, catalyst supports, filters, membrane separation process, catalytic membrane reactors, adsorbents, ceramic foams, entrapment matrices, and precursors for ceramic metal composites, etc.^{1, 34-36} To meet these applications, the elucidation of the microstructure evolution

during heat treatment and the determination of the thermal stability are crucial for the selection of appropriate materials, working conditions and process optimization.

Traditional ceramic processing was performed at high temperature to transform inorganic powders into dense objects by melting or sintering. The high temperatures and agglomeration of powders often limit the control of the properties, microstructure, surface features, and shape obtained. The sol-gel route uses low temperature chemical processes to produce net-shape, net-surface objects, films, fibers, particulates, or composites that can be developed commercially after a minimum number of additional processing steps.³⁷ Moreover, the sol-gel method appears to be particularly attractive to produce porous oxide materials since the process is carried out in a liquid phase at near ambient temperatures, therefore the energy consumption is minimal and safe towards environment.

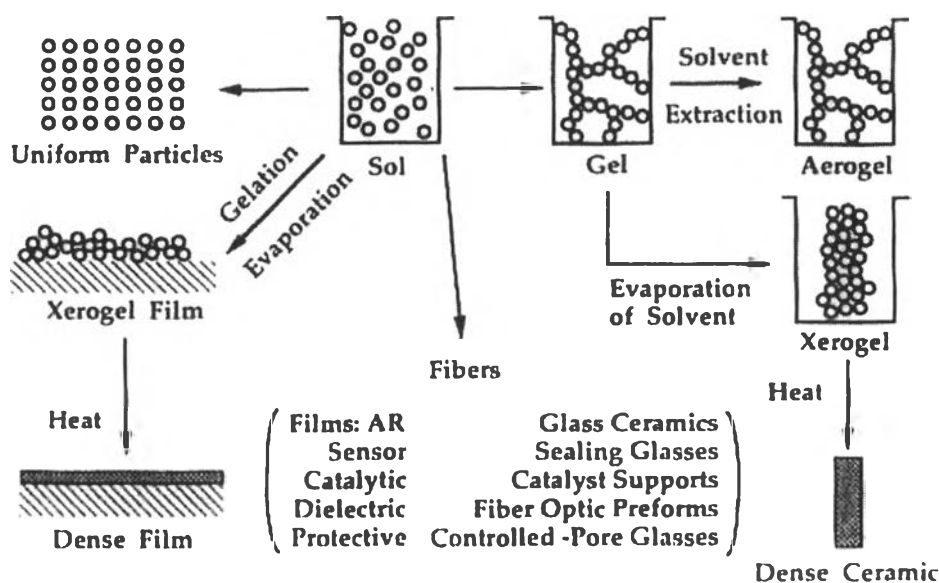


Figure 1. Overview of the sol-gel process.¹

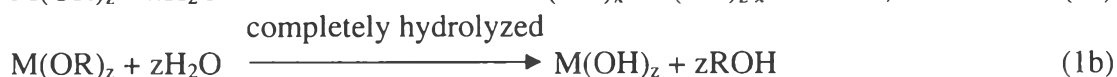
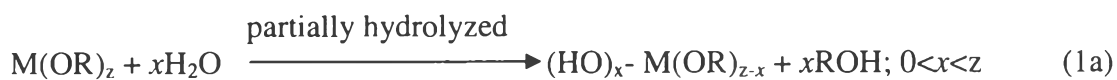
1.2 Sol-Gel Chemistry and Technology

Sol-gel technology in relation to materials chemistry has been extensively investigated and used to explore new approaches in obtaining oxide materials with

improved properties. Additionally, it has evolved through a variety of chemical techniques in controlling the solution chemistry and gelation environment, enabling the properties of ceramic products to be engineered for specific applications.

The traditional sol-gel processing method, sometimes referred to as the 'inorganic route', involves the use of inorganic salts to generate a sol, a suspension of particles in a liquid, which is converted into a gel and further processed to give the oxide.³⁸⁻³⁹ The method which has become increasingly popular in recent times is based on the use of metal-organic complexes in organic solvents as chemical precursors to ceramic oxides. The chemistry of sol-gel preparation involves the formation of a sol followed by the formation of a gel. The precursors or starting compounds for preparation of a colloid consist of a metal or a metalloid element surrounded by various ligands. These are metal salts and metal alkoxides. The latter is the class of precursors most widely used in sol-gel technology. Sol-gel process involves two major reactions: hydrolysis (Eq. (1a) and (1b)) and condensation (Eq. (2a) and (2b)).⁴⁰

Hydrolysis



Condensation



where R is typically an alkyl group, M is the required metallic cations and z is the valence of cations. These reactions can be controlled by adjusting the process parameters, such as hydrolysis ratio, pH conditions, reaction temperatures, the form and the composition of precursor materials.⁴¹⁻⁴³

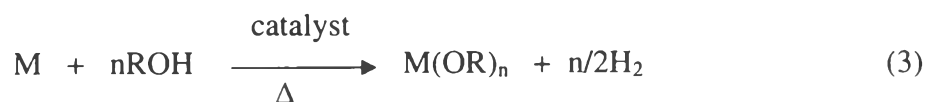
Metal alkoxides have the basic formula of $M(OR)_n$. They are considered to be derivatives of alcohols (ROH) in which the hydroxylic hydrogen is replaced by metals M. Metal alkoxides are easily hydrolyzed and yield oxides, hydroxides and hydrated oxides in a crystalline or amorphous form.

1.3 Precursor Chemistry

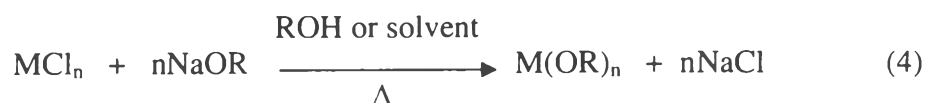
The development of sol-gel precursors relies on the availability of a wide variety of chemical precursors. For some elements, suitable compounds are available commercially and are widely used in industry (e.g. silicon, aluminum, and titanium alkoxides). Metal alkoxides, in particular, fall into this category partly because of their sensitivity to moisture but also because they can undergo a slow condensation reaction on storage to give large polynuclear alkoxo complexes which are no longer soluble in the desired solvents.

Various methods can be used to prepare metal alkoxides.⁴⁴⁻⁴⁵ These methods include:

- (i) Reactions between a metal and an alcohol



- (ii) Reactions between a metal halide and an alkali metal alkoxide

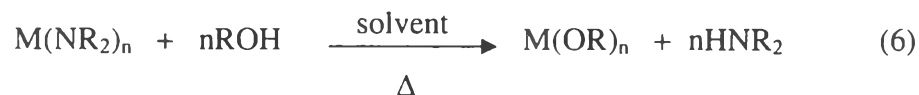


Solvent = toluene, benzene, hexane, etc.

- (iii) Reactions between metal halides and an alcohol in the presence of a base



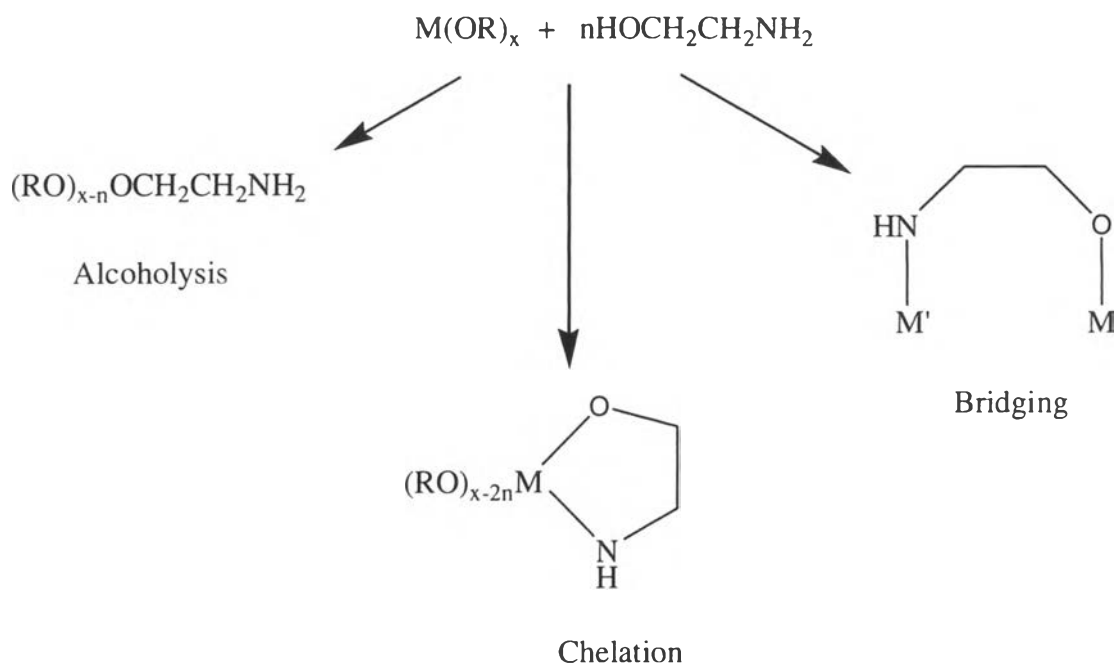
(iv) Reactions of metal amides with alcohols



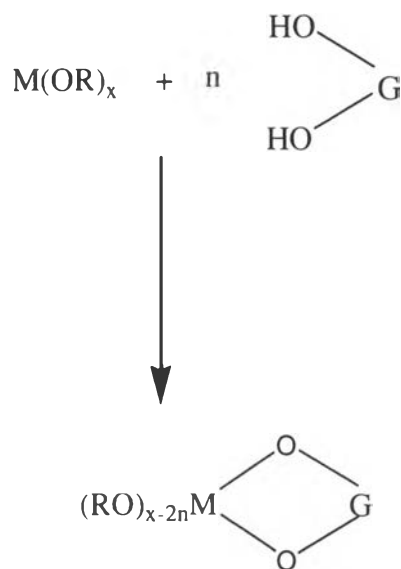
Simple metal alkoxides are thermodynamically unstable in aqueous solution. They usually react readily with water to form precipitates, exception made from those of the relatively more electronegative elements. In fact, the hydrolytic inertness of the alkoxysilanes is the reason for which their chemistry has been the most widely exploited in the preparation of gels, nanoparticles and mesoporous materials. It seems clear, therefore, that controlling the alkoxides reactivity towards the nucleophilic attack of water is an essential requirement for their applicability as precursors of gels or mesostructured materials. It is known that the alkoxides inertness increases with both the size of the organic radicals (steric effect) and the number of alcohol groups in the ligand (chelate or cage effect).^{1, 7, 46} Therefore, the candidates for ligands to construct adequate precursors belong to the series of functionalized polyalcohol.⁴⁷⁻⁴⁸

A variety of additives are often added to metal alkoxide solutions either to stabilize them against differential precipitation of metal hydroxides or to control the hydrolysis rate during the processing stage. They include acids such as carboxylic acids, acetylacetone, bases (amines and alkanolamines), simple alcohols and polyalcohols.^{7,36,39,44} Many of these additives have the potential to bind to the metal centres either as monodentate, chelating or bridging groups. Common binding modes of ethanol amine and glycol are shown in Schemes 1 and 2.

Scheme I



Scheme II



(G stands for the alkyl and alkylene groups)

Metallatranes, or simply atranes, are intramolecular complex cyclic ester or alkoxides of tris(2-hydroxyalkyl)amines having a skeleton of general structure I (Scheme III).

Scheme III



where M is an n -valent element having inorganic or organic substituents when $n > 3$. The term metallatranes, proposed by Voronkov *et al.* (1965), is an abbreviation for the name of aminotrialkoxy derivatives of different elements which contain the above skeleton (I): so aminotrialkoxysilanes give “silatranes”, etc.⁴⁹

The simplest alumatrane, $\text{Al}(\text{OCH}_2\text{CH}_2)_3\text{N}$, was prepared in high yield by the reaction of aluminium alkoxide with triethanolamine in an aromatic solvent (benzene⁵⁰, toluene⁵¹) or with no solvent⁵¹⁻⁵⁵:



Transesterification of aluminium isopropoxide by tris(6-hydroxyhexyl)amine in toluene affords a cyclic ether.⁵¹ Triethanolamine cleaves the Al-C bonds in triethylaluminium in toluene or hexane at -78°C to form alumatrane⁵⁶:



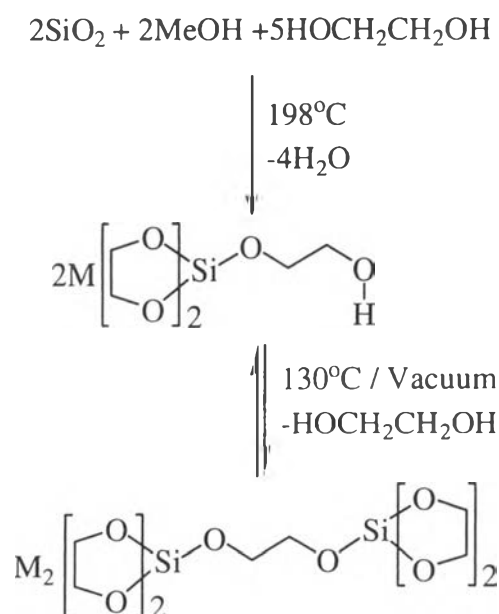
In case of the chelated glycolate ligands, Frye (1969) prepared spiro-siloxane from $\text{Si}(\text{OEt})_4$ and ethylene glycol in ethanol with a small amount of NaOMe. The resulting product was polymeric species, and in the presence of amine bases novel pentacoordinated species would be formed.⁵⁷⁻⁵⁹

In recent years, many synthetic ways have been developed for a wide variety of inexpensive preceramic polymers directly from the metal oxides or hydroxides. One of them, called the “oxide one pot synthesis (OOPS)” process, is very simple and straight-forward.⁶⁰ Reactions between oxides or hydroxides and polyols or aminoalcohols (eg. triethanolamine) can also be costly effective routes to new metal alkoxides of some elements. Moreover, most of work on this area of research has been carried out using Si, Al, and Ti metals with the chelate diol.²¹⁻²⁹

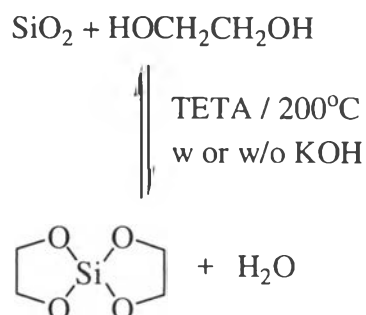
Laine *et al.*(1991) investigated a straightforward, low-cost route to alkoxide precursors by direct reactions of a stoichiometric mixture of silica and group I metal hydroxide with ethylene glycol. This route, termed the ‘oxide one pot synthesis’ (OOPS) process, provides processable precursors, as shown in Scheme IV.²¹⁻²³

Recently, Jitchum *et al.* (2001) synthesized neutral alkoxy silanes, tetracoordinated spiro silicates, directly from silica and ethylene glycol or ethylene glycol derivatives, using triethylenetetramine as catalyst, in the absence or presence of potassium hydroxide as co-catalyst (Scheme V).²⁴

Scheme IV



Scheme V



Interestingly, metal derivatives of glycol are comparatively more hydrolytic resistant than their alkoxide analogues. The chelating nature of the glycol and coordinative saturation achieved by the central atoms in the final products appear to be the main factor for their hydrolytic stability.¹⁷

1.4 The Scope of the Present Work

Although many researchers have solved the problems of high sensitivity of simple metal alkoxides by modifying them to reduce hydrolytic reactivity towards water or moisture in order to avoid a precipitate formation. However, the modifications are rather complicated and expensive. Therefore, the synthesis of new metal alkoxides possessing unique structures and properties is important for the study of sol-gel processes and the evolution of metal alkoxide chemistry.

In other words, the present work stands on the molecular designs and synthesis of novel metal alkoxides.

To achieve the above goals, the present dissertation is divided into three major parts:

- (i) to synthesize and characterize new metal alkoxides, alumatrane, sodium glycozirconate and cerium glycolate complexes which are used further as precursors in sol-gel processes.

- (ii) to study the sol-gel transition of our synthesized metal alkoxides:, sodium glycozirconate, cerium glycolate complexes, and alumatrane and to investigate the effects of parameters in the sol-gel processing on the obtained powders.
- (iii) to prepare and characterize the resulting porous materials derived from the sol-gel processes.

Therefore,

Chapter II is based on the efforts to synthesize other transition metalloglycolates to be used as metal alkoxide precursors in the sol-gel study.

Chapter III deals with the synthesis of alumatrane precursor and the study of the sol-gel transition and the preparation of alumina materials prepared from the alumatrane precursor

Chapter IV is the study of the sol-gel transition and the preparation of zirconia materials obtained from the sodium tris(glycozirconate) precursor

Chapter V is based on the use of the sodium tris(glycozirconate) complex as a precursor for preparing zirconia materials by varying the hydrolysis ratio and the calcination temperature.

Chapter VI deals with the study of hydrolysis during the sol-gel process of the cerium glycolate complex and the use of cerium glycolate complex as precursor for preparing ceria materials by varying the hydrolysis ratio and the calcination temperature.