CHAPTER II
LITERATURE SURVEY

2.1 Synthesis of Metal Alkoxides

Because the precursor in the sol-gei process was quite expensive, this research is tried to synthesize a new precursor of tin oxide. We found that the oxidation number of tin is 4 similarly to titanium so we duplicate experiment of titanium glycolate (Phonthammachai, 2003) prepared by using low cost starting material, titanium dioxide and ethylene glycol and having triethylenetetramine as a catalyst. The synthesis was carried out using Oxide One Pot Synthesis (OOPS method). The ethylene glycol is used as a solvent as well as a reactant material. The obtained alkoxide precursor containing ethylene glycolate ligands is hydrolytically stable, thus yielding more controllable chemistry and minimizing special handling requirement.

In 1996, T. M.Racheve and G. W. Critchlow reported the results from SnO_2 films produced b the sol-gel technique from an alcoholic solution of tin alkoxide ($Sn(OC_2H_5)_4 2\ C_2H_5OH$) as the precursor. Tin (IV) alkoxide ($Sn(OC_2H_5)_4 2\ C_2H_5OH$) was prepared by the reaction of tin (IV) chloride with sodium ethoxide in ethanol. The crystals of ($Sn(OC_2H_5)_4 2\ C_2H_5OH$) were produced. This was used as the starting material for preparation of SnO_2 films by the sol-gel process. After heating and annealing (in the range 500^0C to 700^0C dependent upon the substrate) films were successfully obtained on oxidized silicon, glass and ceramic-glass substrate. The deposited films were converted from being amorphous to being polcystalline with a very small grain size. Carbon could only be detected within the film on the glass substrate whilst sodium was detected at level of between ~2.5-4% in films on both oxidized silicon and plain glass. The sensitivity of these films to variations in humidity was established for values in the range 0% to 93 % relative humidity.

In 2000, Martine Verdenelli and et al prepared new tin oxide precursor for the sol-gel process, $Sn(OEt)_2(\eta^2\text{-acac})_2$ and $Sn_4(\mu_3\text{- }O)_2(\mu_2\text{-}OEt)_6(\eta^2\text{-acac})_2$. These species are of great interest because ethanol is one of the most commonly used

solvent for the sol-gel process. The presence of β-diketone to ligands in the coordination sphere of metal induces the stabilization of the precursor toward hydrolsis reaction, thus permitting the preparation of stable sols or gel with higher hydrolysis ratios. In this work they report the synthesis and structural characterizaton of tin (IV) modified alkoxide with β-diketone: $Sn(OEt)_2(\eta^2\text{-acac})_2$ and $Sn_4(\mu_3\text{- }O)_2(\mu_2\text{-}OEt)_6(\eta^2\text{-acac})_2$.

In 2004, Bussarin Ksapabutr and et al successfully synthesized bimetallic glycolato zirconate ($Na_2Zr(C_2H_4O_2)$) and homometallic glycolato cerate ($Ce(C_2H_4O_2)$, which can be used as alkoxide precursor for sodium zirconium oxide (and/or zirconai by sol-gel) and ceria materials, has been developed from the reaction of inexpensive starting material via the oxide one-pot synthesis (OOPS) process. Both complexes were directly synthesized from zirconium hydroxide/cerium hydroxide and ethylene glycol using base as catalyst. Sodium hydroxide was used in the synthesis of sodium tris(glycozirconate) complex while both triethylenetramine(TETA) as catalyst and trace amout of sodium hydroxide as co-catalyst were used in the case of cerium glycolate complex. The structures of obtained products were investigated using FTIR, TGA, DSC, ^1H and ^{13}C NMR, elemental analyses, EDS and mass spectroscopy. Prolysis studied delineate effect of temperature on the decomposition processes whereby sodium tris(glycozirconate and cerium glycolate precursors transform into $Na_2O.ZrO_2$ and CeO_2, respectively The resulting sodium zirconium oxide and ceria, after pyrolysis at 600°C for 3 h, had BET surface areas of about 62 and 70 m2g-1, respectively, and show monomodal pore size distributions in the mesopore region.

2.2 Synthesis of Tin Oxide

Zhang et al. (2004) synthesized nanocrystalline tin oxide particle by sol-gel method using very simple starting material granulated tin as a precursor. The synthesis led to a sol-gel process when citric acid is introduced in the solution obtained by dissolving granulated tin in HNO_3. Monodispersed SnO_2 nanocrystallites ranging from 2.8 to 5.1 nm in size and 289-143 m^2g^{-1} in specific surface area were

obtained when the gel was given heat-treatment at different temperatures. They found that for citric acid the hydrolysis and condensation were very fast, and comparatively larger and heavier agglomerated SnO_2 nanocrystallites were formed.

Santos et al. (2004) prepared re-dispersible tin oxide nanoparticles by using Tiron molecule ($(OH)_2C_5H_2(SO_3Na)_2$) as surface area modifying agent. The adsorption isotherm measurements showed that an amount of 10 wt% of Tiron was needed to recover the SnO_2 nanoparticle surface with a monolayer. These nanoparticles can be easily redispersed in tetramethylammonium hydroxide at pH≥11 until obtaining a powder concentration of 12 vol.% of tin. Under these conditions, hydrodynamic particle size was about 7 nm and increased until 52 nm at pH 6 due to the aggregation phenomenon. The time evolution of the viscoelastic properties indicated that the suspensions at pH 12.5, containing 12 vol.% tin oxide and 10 wt% of surface modifier were kinetically stable. After thermal treatment at different temperature the powder characterization evidences that the presence of Tiron monolayer at the nanoparticle surface increased the thermal stability of the porous texture and prevented the micropore size growth. This set of results contributed to satisfy the demand for more controlled synthesis of nanoparticles with high thermal stability as required for fabrication of ultra-filtration ceramic membranes.

Wang et al. (2001) synthesized mesostructured SnO_2 using a cationic surfactant (cetyltrimethylammonium bromide,CTAB) as the organic supramolecular template and the hydrous tin chloride ($SnCl_4.5H2O$) in NH_4OH as the inorganic precursor and couterion source under acidic conditions at room temperature. XRD patterns showed that tin oxide assembled with CTAB contained the low angle reflection. The formation of the tin oxide mesostructured material was proposed due to the presence of the hydrogen bonding interaction between supramolecular template and inorganic precursors Sn^{4+} and OH^-, which were supposed to self-assemble around the cationic surfactant molecules.