<u>Spinel preparation</u>

1. <u>Oxide One Pot Synthesis (OOPS) process</u>

A process that has gained much notoriety in preceramic polymer fields is the Oxide One Pot Synthesis (OOPS)" process first discovered by Laine in 1996 and has been extensively studied in the last ten years (Waldner *et al*, 1996). This synthetic route produces a variety of new chemicals, polymers and ceramics from metal oxides or hydroxides. The process involves preceramic polymer formation by chemical reaction in one step. Through this chemical route, homogenous inorganic oxide materials with desirable properties of purity, homogeneity, can be produced at lower temperature compared to conventional oxide mixing method. Many preceramic polymers are synthesized directly from the corresponding metal oxides or hydroxides and have been described in previous reports (Wongkasemjit and Laobuthee, 2001). The specific used of this Oxide One Pot Synthesis (OOPS) process produced ceramics which can be transformed to the various materials shapes such as thin films, fibers and monosized powders. Many specific applications include refractory, fusion reactor power core insulating, composite, electroceramic and ion exchange materials, electronic humidity and automotive gas sensors, catalysts, catalytic supports and promoters in several industrial catalytic processes, optical coating, reinforcement fibers and absorbates.

Recently, an inexpensive spinel double alkoxide precursor, composed of aluminium, magnesium with triethanolamine [$N(CH_2CH_2OH)_3$, TEA] as ligating molecule is readily produced. The reaction is performed via OOPS process based on the following reaction, using ethylene glycol (EG) as solvent.

$$200^{\circ}C \ /-H_2O$$

$$2Al(OH)_3 + MgO + 3TEA + x^{\prime} \ EG \longrightarrow$$

...(1)
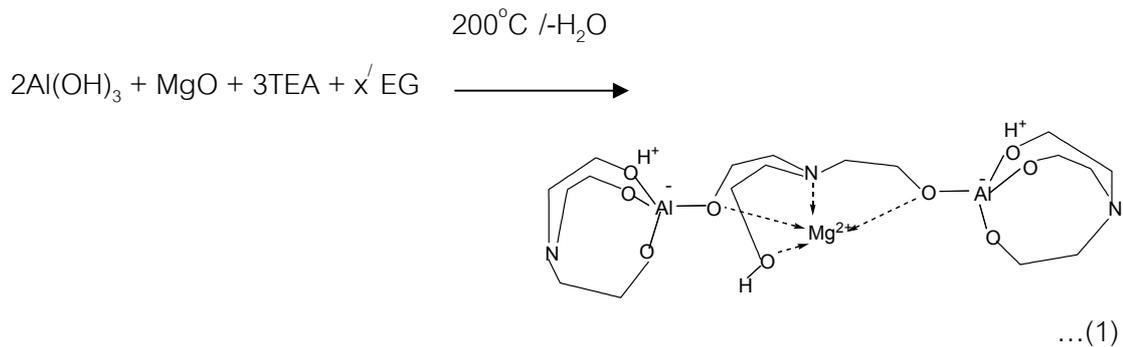
The spinel precursor is converted to spinel powder by pyrolyzing which could be characterized by XRD.

Up to now, there are many researchers developed synthetic routes to a wide variety of inexpensive preceramic oligomer alkoxides by Oxide One Pot Synthesis (OOPS) process.

Laine *et al*. (1996) developed the process to make aluminosilicate precursors. The "Oxide One Pot Synthesis process", a mixture of SiO_2, $Al(OH)_3$ and a group I/II hydroxide/oxide, in any stoichiometric ratio, is reacted with one mole of triethanolamine ($TEAH_3$) per mole of metal, by heating in ethylene glycol (EGH_2) such that the by product H_2O distills off. Solvent removal provides relatively moisture- and air-stable viscous, polymer-like precursors that probably consist of silatrane (TEASi-EGH) and alumatrane [(TEAAl)$_4$] complexes. Spinel, mullite and cordierite precursor syntheses are described. The mullite and cordierite precursors most probably are homogenous mixtures of single-metal alkoxides rather than atomically mixed, bi- and tri-metallic alkoxides. The precursors are soluble common solvents, and offer viscoelastic properties suitable for powder, coating and fiber spinning applications. Pyrolysis (in air) to $\geq 700^{\circ}C$ provides glass or ceramic materials with exactly the stoichiometry of the starting oxide mixture.

Waldner *et al*. (1996) synthesized $MgAl_2O_4$ directly from $Al(OH)_3$ and MgO or $Mg(OH)_2$ with triethanolamine, [TEA, $N(CH_2CH_2OH)_3$] in ethylene glycol (EG) provided, in one step, access to a polymer-like precursor to spinel. On the basis of high-resolution mass spectroscopy, chemical analysis and ^{27}Al solution NMR, the precursor appears to be a trimetallic double alkoxides consisting of two four-coordinate TEAAl (alumatrane) moieties linked via a bridging TEA group that enfolds the Mg cation. The ^{27}Al NMR shows only tetracoordinate Al centers (64.8 ppm). The same compound can be prepared stepwise by reaction of tetrameric alumatrane, $(TEAAl)_4$, with Mg and TEA. Product evolution upon pyrolysis was followed as a function of temperature using TGA, DTA, XRD, and diffuse reflectance infrared spectroscopy (DRIFTS). Pyrolysis at 700^oC for 2 h in air appears to produce a γ- Al_2O_3- $MgAl_2O_4$ solid solution and small amount (< 5 wt %, by TGA) of X-ray amorphous $MgCO_3$. Transformation of the solid solution to pure spinel is a function of pyrolysis temperature and time, with only spinel evident in the XRD data, after pyrolysis at 1200^oC for 2 h. BET analysis of the pyrolysis products gave surface areas as high as 160 m^2/g (500 ^oC/2h/air). Porosimetry reveals a bimodal distribution of micropores centered around 10 and 60 Å, accounting for the majority of the surface area. The powder morphology was briefly examined using SEM.

Wongkasemjit and Laobuthee (2001) studied the preparation of spinel powder by various chemical techniques, such as Oxide One Pot Synthesis (OOPS) process, mixed oxide route and from alumatrane and $Mg(OMe)_2$. The oligomer-like precursor to $MgAl_2O_4$ spinel has been developed and successfully synthesized in one step directly from $Al(OH)_3$ and MgO with triethanolamine, [TEA, $N(CH_2CH_2OH)_3$] in ethylene glycol solvent or from the reaction of alumatrane and magnesium methoxide. The precursors were converted to spinel by pyrolyzing at 1100^oC for 2 h in air. Characterization was carried out using NMR, XRD and SEM. As compared both simple and straightforward synthetic route, they offered more advantages, such as shorter processing times, higher homogeneity and higher product purity.

Phonthammachai *et al*. (2002) investigated a much milder, simpler and more straightforward reaction to produce titanium glycolate by the reaction of titanium dioxide, ethylene glycol and triethylenetetramine using the Oxide One Pot Synthesis (OOPS) process. The FT-IR spectrum demonstrates the characteristics of titanium glycolate at 619 and 1080 cm^{-1} assigned to Ti-O stretching and C-O-Ti stretching vibration, respectively. C-solid state NMR spectrum gives two peaks at 75.9 and 79.8 ppm due to the relaxation of the crystalline spirotitanate product. The percentage of carbon and hydrogen from elemental analysis are 28.6 and 4.8, respectively. The thermal analysis study from TGA exhibits only one sharp transition at 340°C corresponding to the decomposition transition of an organic ligand, and giving a ceramic yield, titanium glycolate, of 46.95% which is close to the theoretical yield of 47.50%. XRD patterns show the morphology change of its pyrolyzed product from anatase to rutile with increasing calcining temperatures from 500°C to 1100°C while at 300°C the amorphous phase is formed.

Thanabodeekij *et al*. (2003) prepared a very high purity $MgAl_2O_4$ spinel precursor via a low temperature process called "Oxide One Pot Synthesis (OOPS)". Sol-gel processing of such precursors offers the opportunity to prepare spinels with controlled microstructures, which is key to optimizing their properties for application as humidity sensors. Sol-gel processing of a double alkoxide precursor was carried out in buffer solutions in the pH 8-12, to investigate the effect on the physical properties of the calcined ceramic products. The structure and morphology of the latter were characterized using FTIR, XRD, SEM and BET surface area measurements. Sol-gel processing results in a calcined product with a narrow pore size distribution, which contains a spinel phase of high crystallinity. At higher pH values, increasing amounts of an α- Al_2O_3 phase are formed. At all pH values the calcined product exhibits high water adsorption, up to 0.312 g H_2O/g sample.

Ksapabutr *et al*. (2004) prepared zirconia powders by a sol-gel method, using sodium glycozirconate complex as precursor synthesized via the Oxide One Pot Synthesis (OOPS) process. Gelation of this precursor was achieved through the variation of the hydrolysis ratio without the use of the dopants. The gel samples were also calcined at different temperatures. The resulting zirconia was characterized using X-ray diffraction (XRD), SEM and nitrogen adsorption/desorption. The solid materials obtained after heat treatment at 500°C by varying the hydrolysis ratio have large surface areas of 154-220 m^2/g and a narrow pore size distribution in the mesopore region. By variation of the heat treatment, the zirconia xerogels existed in either an amorphous, tetragonal, or monoclinic form at room temperature. Based on XRD data the first identifiable crystalline structure from the amorphous phase was the tetragonal polymorph, which was formed between 500 and 800°C. When the temperature was raised to 1000°C, zirconia powder with a monoclinic structure was obtained. Surface areas about 280 m^2/g was obtained after calcination at 400°C, which drop to ca. 70 m^2/g following treatment at 1000°C.

2. Sol Gel Process (Ertl *et al*., 2001)

The Sol-Gel process allows to synthesize ceramic materials of high purity and homogeneity by means of preparation techniques different from the traditional process of fusion of oxides. This process involves first the formation of a sol followed by that of a gel. The sol is made of solid particles with a diameter of few hundred nanometer suspended in a liquid phase. Then the particles condense in a new phase (Gel) in which a solid macromolecule is immersed in a liquid phase (solvent). Drying the gel by means of low temperature treatments (25-100°C), it is possible to obtain porous solid matrices (Xerogels). The fundamental property of the sol-gel process is that it is possible to generate ceramic material at a temperature close to room temperature. Therefore such a procedure opened the possibility of incorporating in these glasses soft dopants, such as fluorescent dye molecules and organic chromophores.

The single most important characteristic of the sol-gel preparation of catalytic materials is its ease of control that the advantages translate into the ability to maintain high purity (because of purity of starting materials), change physical characteristics such as pore size distribution and pore volume, vary compositional homogeneity at a molecular level, prepare samples at low temperatures, introduce several components in a single step and produce samples in different physical forms.

2.1 Important Parameters in Sol-Gel Preparation

Figure 4 shows the four key steps in taking a precursor to particular product form via sol-gel preparation: formation of a gel, aging of a gel, removal of solvent, and heat treatment. The versatility of this preparative approach lies in the number of parameters that can be manipulated in each of these steps.
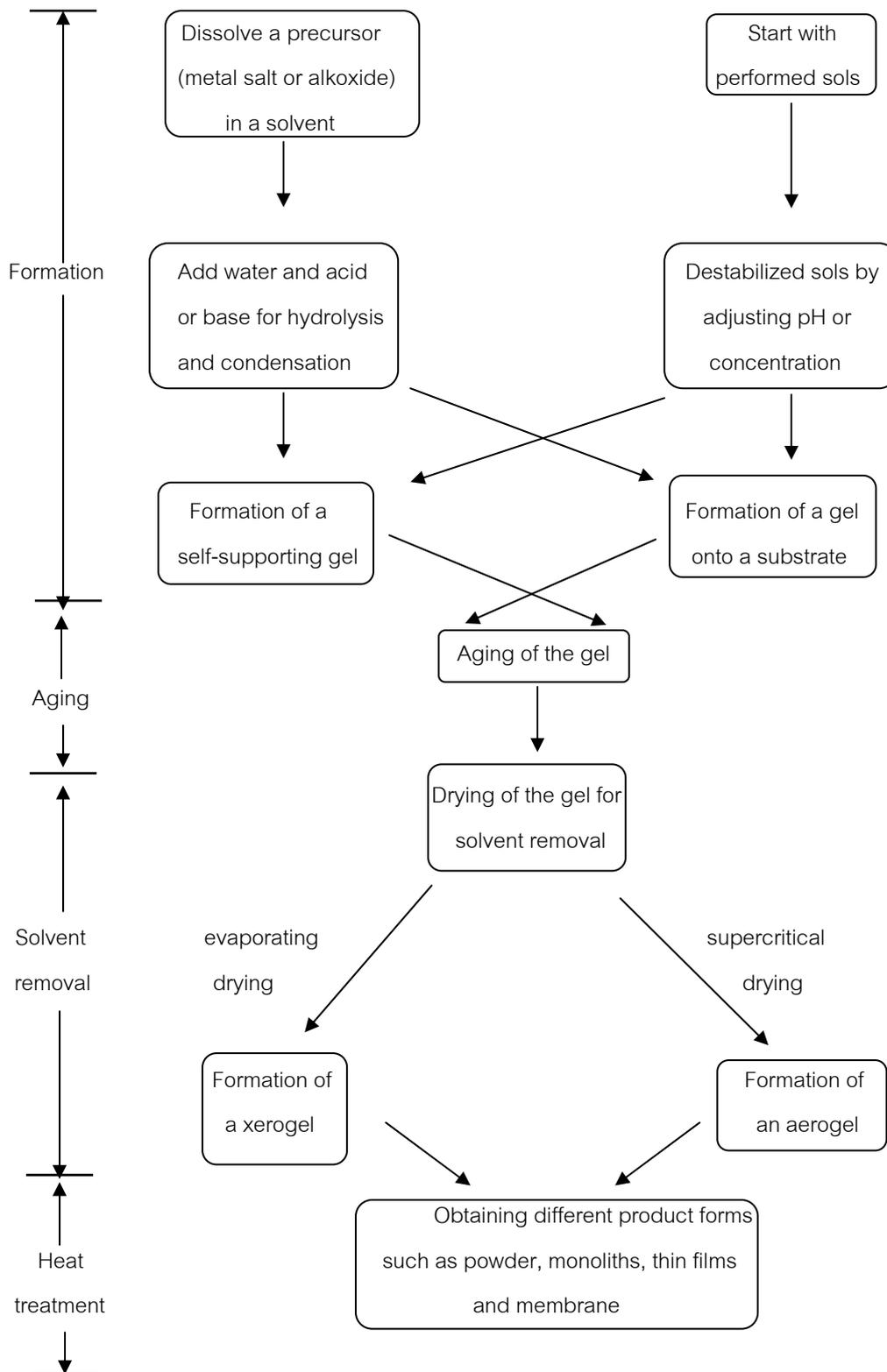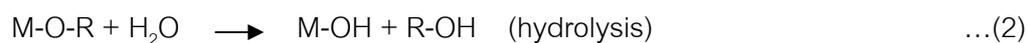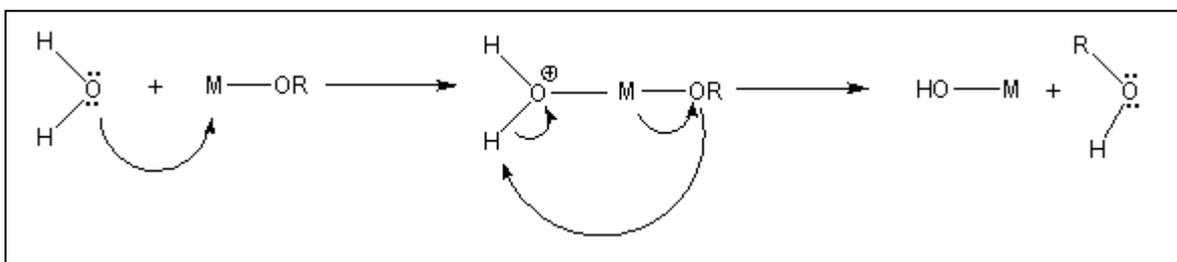
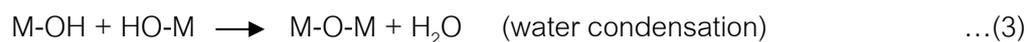Figure 4 Schematic diagram showing the various steps of a sol-gel process.

Source: Ertl *et al*. (2001)
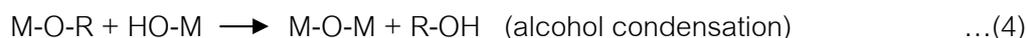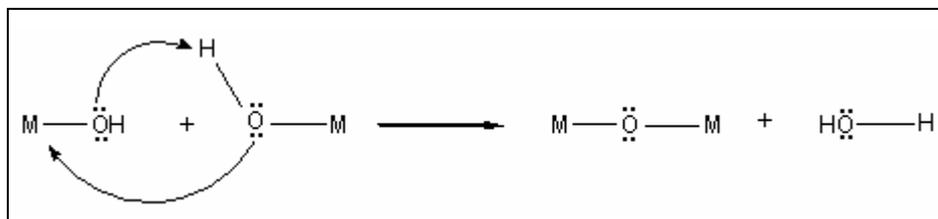
2.1.1 Solution Chemistry

This process occurs in liquid solution of organometallic precursors, which by means of hydrolysis and condensation reactions, lead to the formation of a new phase (SOL).

$$M\text{-}O\text{-}R + H_2O \longrightarrow M\text{-}OH + R\text{-}OH \quad \text{(hydrolysis)} \qquad \dots(2)$$

Hydrolysis mechanism

Consequently, the chemical reactivity of metal alkoxides toward nucleophilic reactions mainly depends on the strength of the nucleophile, the electrophilic character of the metal atom (an electronegativity-related property characterized by the positive charge on the metal atom) and its ability to increase its coordination number N : the degree of unsaturation of the metal coordination can be simply expressed by the difference N-Z, where N is the coordination number usually found in the oxide and Z is the oxidation state.

$$M\text{-}OH + HO\text{-}M \longrightarrow M\text{-}O\text{-}M + H_2O \quad \text{(water condensation)} \qquad \dots(3)$$

Water condensation mechanism

$$M\text{-}O\text{-}R + HO\text{-}M \longrightarrow M\text{-}O\text{-}M + R\text{-}OH \quad \text{(alcohol condensation)} \qquad \ldots(4)$$

Alcohol condensation mechanism
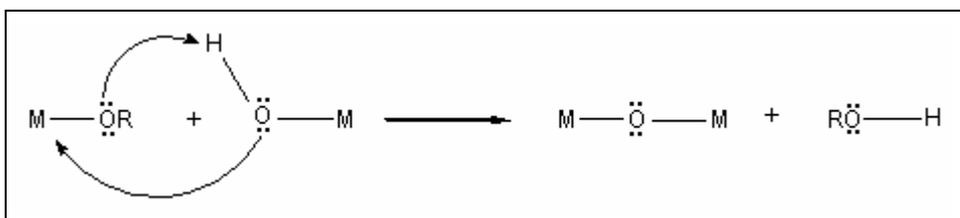
(M = metal)

       Such a description oversimplifies the overall process because it does not correctly represent the molecular formulas of the intermediates and end products, nor does it depict the simultaneous occurrence of the two reactions. However, this oversimplification captures the key phenomenological idea that a three-dimensional gel network comes from the condensation of partially hydrolyzed species. Any parameters that affect either or both of these reactions are thus likely to impact on the properties of the product. In fact, Livage *et al.* pointed out that the important variables are the relative rates of hydrolysis and condensation.

       Figure 5 shows the rates of hydrolysis and condensation of tetraethylorthosilicate (TEOS), which is the most widely studied precursor, vary as a function of pH. Under acidic conditions hydrolysis occurs at a faster rate than condensation and the resulting gel is weakly branched (Figure 6). Under basic

conditions, the reverse is true and the resulting gel is highly branched and contains colloidal aggregates (Figure 7). Subsequently dried and heat-treated samples have different surface functionalities and pore structures (Handy *et al.*, 1991).
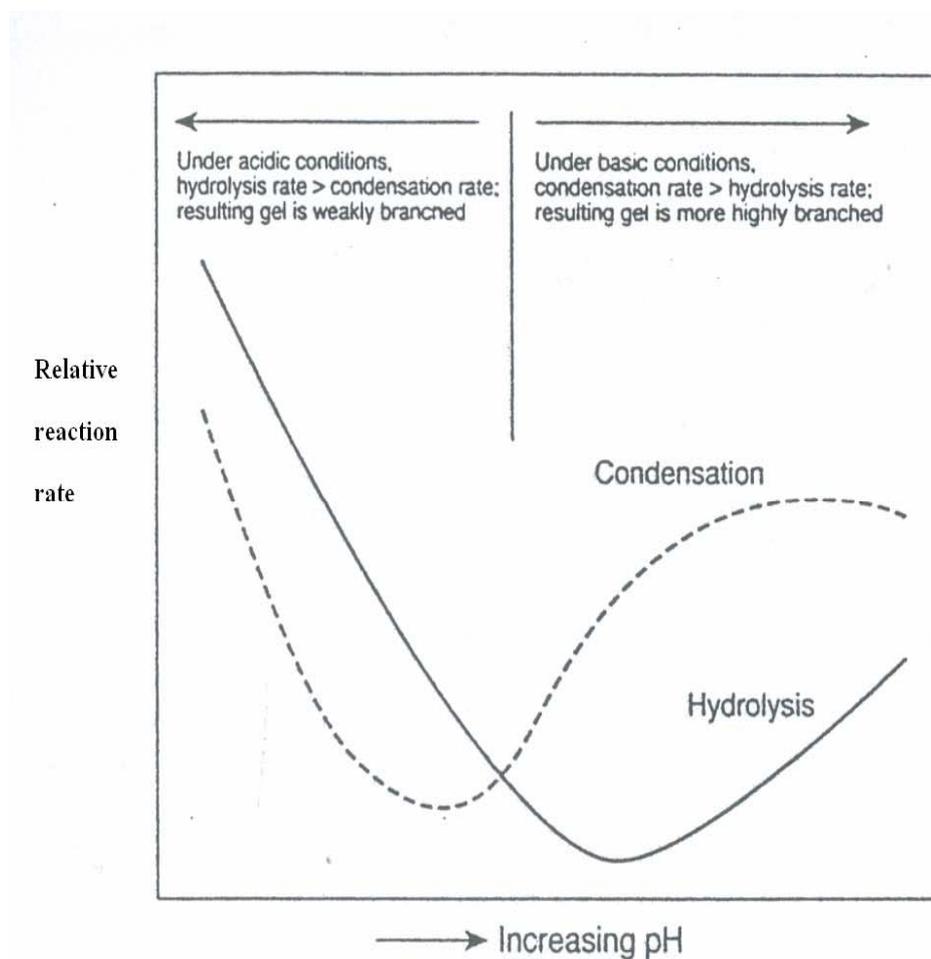
Figure 5 Schematic diagram showing the variation of hydrolysis and condensation rates of tetraethylorthosilicate with pH, and the effect of relative rate on gel structure.

Source: Ertl *et al.* (2001)

SOL
Far from gel point

|←— 100 Å —→|

SOL
Near gel point

entangled primarily
linear macromolecules

GEL POINT

aditional crosslinks
at junctions

Figure 6 Polymer growth and gel formation in acid-catalyzed systems

(polymeric gel)

Source: Zelinski and Uhlmann (1984)

Figure 7 Polymer growth and gel formation in base-catalyzed systems
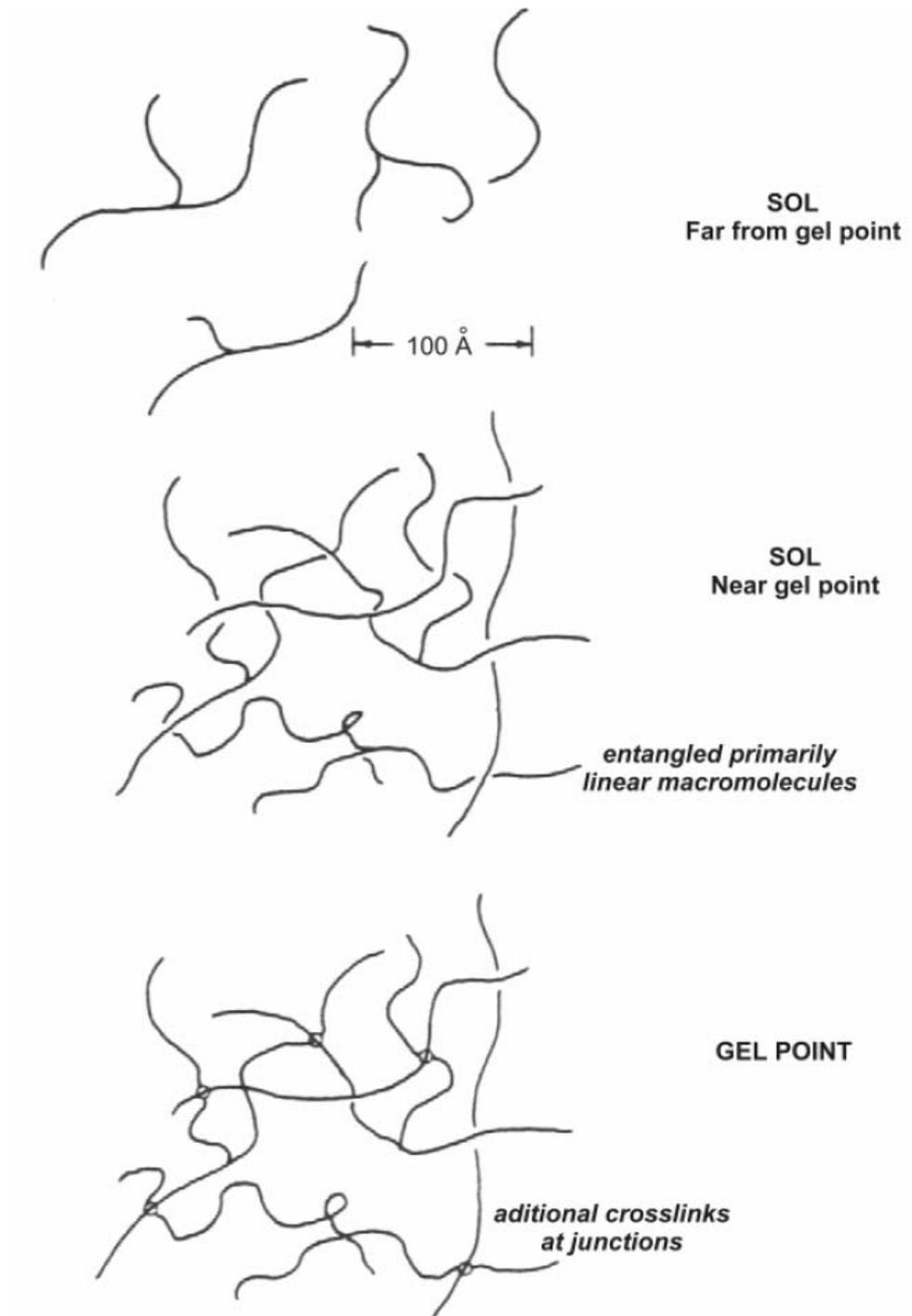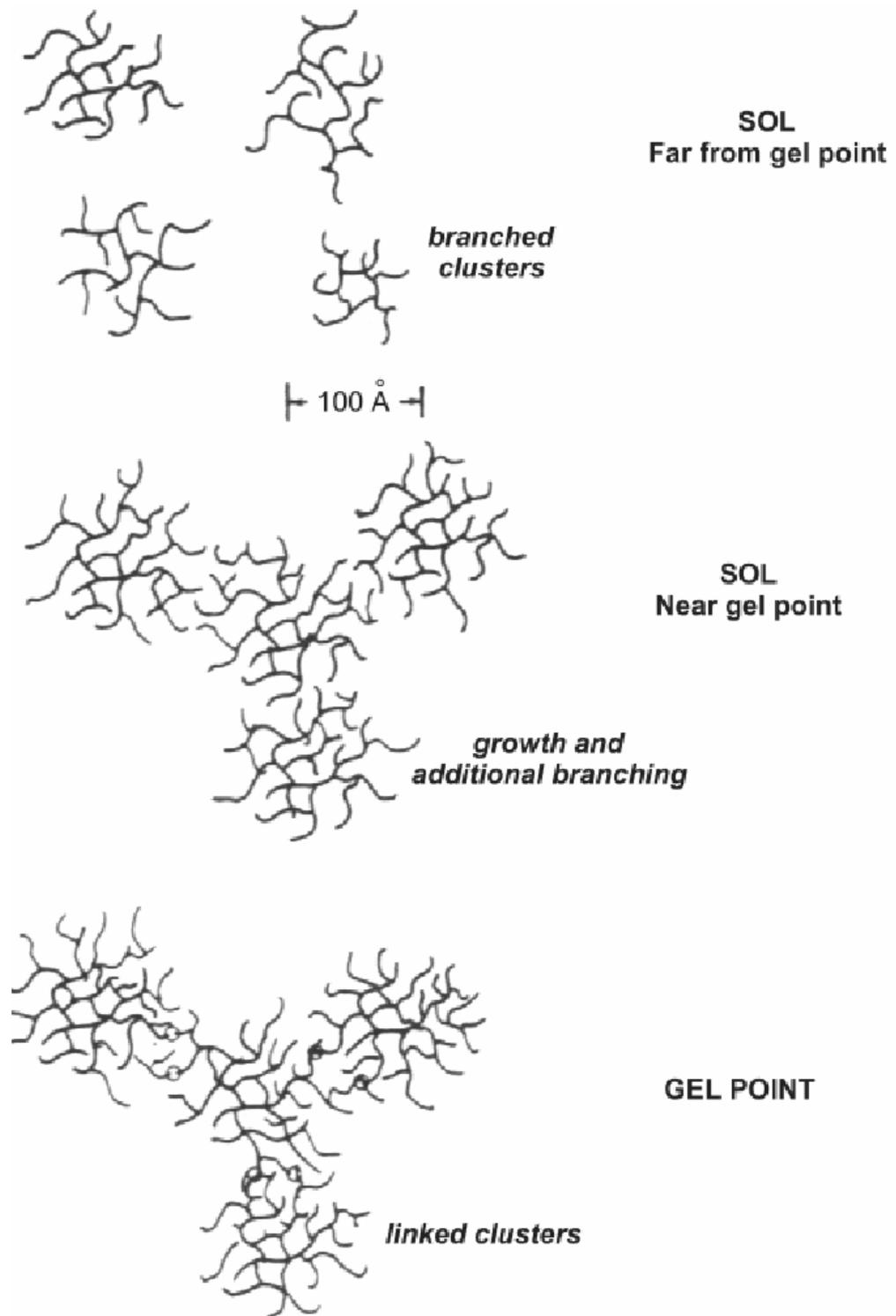
(colloidal gel)

Source: Zelinski and Uhlmann (1984)

Because hydrolysis and condensation are both nucleophilic displacement reactions, the reactivity of metal alkoxides is dependent on the positive partial charge of the metal atom and its coordination number. For example, TOES, with a small positive partial charge on silicon, is the least reactive among the common alkoxides. In general, the longer and bulkier the alkoxide group attached to a particular metal atom, the less reactive that precursor is in hydrolysis and condensation. Changing the type of precursor and/or its concentration are thus effective means of controlling the reaction rates.

The amount of water used in sol-gel preparation and the rate by which it is added also influence gel characteristics. The former is usually expressed in terms of the hydrolysis ratio h, defied as the moles of water per mole of metal alkoxide, $M(OR)_m$. There are three specific regions of interest:

(i) $h < 1$: An infinite network seldom forms due to the low functionality of the precursor towards condensation. Because there are few M-OH groups for cross-linking, gelation or precipitation cannot occur when there is no local excess of water.

(ii) $1 < h < m$: Polymeric gels can form.

(iii) $h > m$: Cross-linked polymers, particulate gels, or precipitates can form when an excess of water is added to the alkoxides.

where, m = number of alkoxide group (-OR)

For a given amount of water, another level of control comes from the rate of addition. Common approaches in adding water slowly are using a

micropipette, absorbing moisture from a controlled humidity environment, and generating water in the solution with another chemical reaction.

Two other important sol-gel parameters are temperature and solvent. Both hot and cold plates are commercially available and can be used to increase and decrease the reaction rates, respectively. Varying the temperature is most effective when it can alter the relative rates of competing reactions. Solvent can change the nature of an alkoxide through solvent exchange or affect the condensation reaction directly. It is also possible to prepare a gel without a solvent as long as another means, such as ultrasound irradiation (Zarzychi, 1992), is used to homogenize an otherwise immiscible alkoxide/water mixture.

2.1.2 Aging

Aging represents the time between the formation of a gel and the removal of solvent. As long as the pore liquid remains in the matrix, a gel is not static and can undergo many transformations (Brinker and Scherer, 1990). For alkoxide derived gels, condensation between surface functional groups continue to occur after the gel point. This process can actually be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handle. However, extensive condensation causes the gel to shrink to the point that solvent is actually expelled, in a phenomenon called syneresis. Coarsening, or ripening, is a physical process driven by differences in solubility associated with surfaces that have different radii of curvature. Coarsening basically involves the dissolution and reprecipitation of particles resulting in as increase in the average pore size of the gel and a decrease in its specific surface area.

Parameters that affect these aging processes include temperature, time, and pH of the pore liquid. Common approaches in manipulating these parameters are immersing the gel to a different humidity, heating the gel, and

using hydrothermal conditions. Even though all these approaches have been demonstrated to change the gel characteristics, an understanding of the cause and effect is at best qualitative at present. For this reason aging is often an overlooked step in the sol-gel preparation of catalytic materials. The recent work of Smith *et al*., who developed an in situ NMR technique for following the aging process, may open up new opportunities in this area.

2.1.3 Drying

The gel drying process consists of removal of water from the gel system, with simultaneous collapse of the gel structure, under conditions of constant temperature, pressure, and humidity.

As the pore liquid is evaporated from a gel network, the capillary pressure associated with the liquid-vapor interface within a pore can become very large for small pores. For example, the capillary pressure with water evaporation from a pore with a radius of 1 nm is in the order of 1.5×10^8 pa. With a distribution of pore sizes in a gel, as is commonly the case, the differential pressure across pores of different sizes leads to a collapse in the pore structure. Thus, strategies those are effective in maintaining the integrity of a gel network aim at minimizing either the differential pressure or the capillary pressure itself.

One approach to minimize capillary pressure is to prepare gels containing uniform-sized pores or at least a narrow pore size distribution. This can be done by adding organics such as formamide and glycerol, which are called drying control chemical additives (DCCA), to control the rates of hydrolysis and condensation and in turn the pore size distribution. There are many examples showing that glasses and ceramics prepared with DCCA can better withstand drying due to a more uniform pressure distribution across the gel network. The use of DCCA in preparing catalytic materials has not been common, partly because there are alternatives that do not

introduce potential impurities into the system. The easiest way to understand approaches that are effective in minimizing the capillary pressure directly is to examine the equation

$$P = 2\sigma \cos(\alpha)/r \qquad \qquad \ldots(5)$$

Where P is capillary pressure, σ is surface tension, α is the contact angle between liquid and solid, and r is the pore radius. For a given pore size, then, the capillary pressure can be reduced by (i) using a solvent with a lower surface tension or with a contact angle close to 90° and (ii) eliminating the liquid-vapor interface altogether with either supercritical or freeze drying.

Smith and co-workers have aged silica gels in either ethanol or water and subsequently washed them in various aprotic solvents that cover a range of surface tensions (Smith *et al.*, 1992). Their results clearly demonstrated the effect of surface tension on microstructure because the resulting xerogels have a wide range of surface area and pore volume. Furthermore, the effect is dependent on the initial network rigidity as acid-catalyzed and base-catalyzed gels respond to the treatment differently. The fact that some of these xerogels have comparable physical properties to aerogels obtained by supercritical drying suggests an attractive alternative in preparing high surface-area, low-density materials at ambient pressure.

Supercritical drying is a high-pressure approach aimed at eliminating the liquid-vapor interface and the accompanying capillary pressure. Since the pioneering work of Kistler, the technology of supercritical drying has evolved from a tedious, multistep process to a simpler and safer semicontinuous process. One major advance came from the group of Teichner who used alcoholic solutions of metal alkoxide in preparing gels with a minimal amount of water. In prior preparations that used a large amount of water, tedious washing and solvent exchange steps were

necessary because water would dissolve the gel structure at high temperatures. There are now numerous examples showing that aerogels can be prepared to give high porosities, high specific surface areas, low apparent densities, and good textural stability. These advantages can be realized because, in addition to elimination the liquid-vapor interface, supercritical drying is done at moderate temperatures. In fact, one often overlooked advantage in supercritical drying is its ability to preserve the amorphous structure of an aerogel. For example, it has been reported that a niobia aerogel is slower to crystallize than a xerogel upon further heat treatment and hence better able to retain its high acid strength along with acid site density.

Similar to aging, a gel is not static during drying and, for that reason, drying can be viewed as part of the overall aging process. The properties of a product are thus dependent on the drying method and even with a single method, the drying conditions. Most supercritical drying experiments have been done with alcohol because of its use as a solvent in the sol-gel step. But ever since supercritical carbon dioxide was shown to be an effective agent for displacing alcohol, many researchers have reported on the effect of drying agent on the properties of aerogels such as silica (Smith *et al.*, 1992), titania, and titania-silica. Because different substances have different critical temperatures, these results can be understood in terms of the accelerated aging of a gel at a higher drying temperature. For example, recently Brodsky and Ko showed that varying the temperature while using a single drying agent, carbon dioxide, can also change the textural and structural properties of calcined titania aerogels. Besides temperature, other parameters that are important in supercritical drying include the path to the critical point, depressurization, and composition of the drying medium. In particular, reduction is prone to occur when an autoclave is filled with hydrogen during drying.

One other approach in bypassing a liquid-vapor interface is freeze drying, in which the pore liquid is frozen into a solid that subsequently sublimes to give a

product called a cryogel. Data on the characteristics of cryogels are limited because freeze drying has not been used as extensively as supercritical drying in preparing catalytic materials

2.1.4 Calcination/Sintering

After the removal of pore liquid, further heat treatment is necessary to convert a xerogel or aerogel into a catalytically useful form. Often, heating is done in the presence of a reactive gas (e.g. flowing air, oxygen, or hydrogen) in order to burn off any residual organics or to oxidize (or reduce) the sample. Exposing the sample to a high temperature over an extended period of time leads to sintering and consequently a decrease in surface area. The process can also cause the material to crystallize into different structural forms. Thus, the physical characteristics of a product depend on parameters such as temperature, heating rate, time, and gaseous environment. It is common practice to subject a sample to a more severe heat treatment that it is likely to encounter in a reactor to ensure at least the stability of its textural and structural properties during reaction.

Table 1 provides a quick reference to the four key steps in a sol-gel process, the purpose of each step, and the associated experimental parameters that can be varied. Since each of these parameters can potentially affect the properties of a product, literature results on sol-gel preparation should be reported or examined in a similar formal to allow a meaningful comparison among different studies

Table 1 Important parameters in the various steps of a sol-gel process

Step	Purpose	Important parameter
Solution chemistry	to form a gel	type of precursor; type of solvent; pH (acid/base content); water content; precursor concentration; temperature
Aging	to allow a gel to undergo changes in properties	time; temperature; composition of the pore liquid (e.g. pH): aging environment (e.g. humidity)
Drying	to remove solvent from a gel	drying method (e.g. evaporative vs supercritical vs. freeze drying); temperature and heating rate; pressure and pressurization rate; time
Calcination/sintering	change the physical/chemical properties of the solid, often resulting in crystallization and densification	temperature and heating rate;time; gaseous environment (e.g. inert vs. reactive gases)

Source: Ertl *et al.* (2001)

Kurihara and Suib (1993) synthesized several ternary metal oxides having the formula MAl_2O_4 where M = Mg, Ni, Co, Cu, Fe, Zn, Mn, Cd, Cu, Hg, Sr, and Ba and the compound $PbAl_2O_5$ with sol-gel methods and compared to materials produced by traditional high-temperature solid-state procedures. These transparent sol-gel materials are crystalline as shown by X-ray diffraction methods. The size and charge of M ions and their corresponding resultant structures are found to be related to crystal field and octahedral stabilization energies. Particle sizes range from 20 to 200μm as determined by scanning electron microscopy experiments. Thermal stability of the $NiAl_2O_4$ material has been studied by differential scanning calorimetry methods. Small metal (M) ions form different structures such as the cubic $PbAl_2O_5$ phase, the hexagonal phase of $BaAl_2O_4$, the monoclinic phase of $CaAl_2O_4$, and the hexagonal $CdAl_2O_4$ and $HgAl_{12}O_{13}$ phases.

Meyer *et al*. (1999) prepared nanocrystalline aluminate spinels with cobalt, nickel or copper as bivalent cations in different particle sizes using *single-source* heterometal alkoxides of the type $[M\{Al(OR)_4\}_2]$ (M^{II} = CO, Ni, Cu; R = Pr^i, Bu^t) in a microemulsion assisted sol-gel process. The compatibility of the metal stoichiometry in the precursor molecules with respect to the spinel requirement was established by elemental, spectroscopic and single crystal X-ray diffraction analyses. Synthesis of $CoAl_2O_4$ using both single- and multi-component routes gave different results: where as the cobalt, nickel or copper as bivalent cations in different particle sizes using single-source precursor approach yielded monophasic high purity spinels, phase contaminate was evident in the diffractograms of ceramics obtained using a mixture of individual components. The alkoxide precursors were hydrolysed in a homogeneous dispersion of colloidal water droplets in a non-aqueous phase. The diameter water droplets in the microemulsion can be turned, *inter alia*, by varying the hydrophilic chain length of the surfactant molecules which influences the size distribution of nanoparticles in the MAl_2O_4 ceramics. This parameter is used to obtain nano-spinels with particles sizes in the range 4-45 nm and reveals a qualitative correlation between the initial droplet size and the crystallite size of

the resulting spinels. The TG-DTA measurements showed the thermal decomposition to be a three step process with crystallisation of the spinel phase ocuuring around $900^{\circ}C$. ^{27}Al MAS NMR spectra reveal the inverse nature of the obtained spinels. XRD, TEM, SEM, EDX, FTIR and UV-VIS spectral studies were used for characterisation of the powders.

Otero Areán *et al*. (2001) prepared the oxide spinel $NiAl_2O_4$ and spinel-type solid solutions Al_2O_3- $NiAl_2O_4$ (at Ni/Al=1:4, and Ni/Al=1:8) by controlled hydrolysis of mixed metal alkoxides, followed by calcination of the resulting gels. Powder X-ray diffraction showed thst all samples prepared were single phase cubic materials having the spinel-type structure. The cubic lattice parameter, a_O, was found to decrease gradually with increasing aluminium content of the mixed metal oxides. The specific surface area (determined by nitrogen adsorption at 77K) was found to be in the range of 200-300 m^2/g. The materials were found to be basically mesoporous, the most frequent pore radius being in the range 3.2-6.4 nm. IR spectroscopy of CO adsorbed at liquid nitrogen temperature gave a main band at 2186-2195 cm^{-1}, which was assigned to the C-O streching vibration of surface $Al^{+3\cdots}CO$ adducts where coordinatively unsaturated Al^{+3} ions act as Lewis acid centres.

Xu *et al*. (2001) prepared a newly designed ultrafine $NiO\text{-}La_2O_3\text{-}Al_2O_3$ aerogel catalyst by the combination of sol-gel method and supercritical drying (SCD) technique for CH_4/CO_2 reforming. Compared to the conventional impregnated catalyst, it exhibits unusual physical and chemical properties, as manifested in very large specific surface area, well-define pore size distribution and good textural stability. Very high activity and at the same time very low carbon deposition were also observed. It more easily forms homogeneously distributed $NiAl_2O_4$ spinel in aerogel catalyst at low heat treatment temperature and has much higher capacity to adsorb CO_2, which may be mainly responsible for its excellent catalytic performance and insensitive to carbon deposition.

Piao *et al.* (2002) prepared an alumina supported nickel aerogel catalyst by the sol-gel method and used in the catalytic decomposition of methane. An in situ thermal balance reactor was employed in the study of the reaction. A number of catalysts prepared by the same procedure with different nickel to aluminium ratio were tested. It has been observed that the catalyst oxide precursor has a $NiAl_2O_4$-like structure. The amount of the carbon nanotubes (CNTs) formed before the deactivation of the catalyst increases with the nickel content in the catalyst. CNTs grow in 450-700°C. TEM micrographs show that the CNTs are curved, with diameters in the range of 10-20nm. Both the reaction and catalyst reduction condition have strong influences on the morphology of the CNTs and on the reaction behavior.

Krompiec *et al.* (2003) synthesized nickel-alumina composite aerogels with large nickel loading using a novel complexing agent-assisted sol gel procedure to obtain materials displaying very large and open internal surface area, easily accessible for large molecules and demonstrating excellent catalytic properties. They were tested in the following reactions: (I) hydrogenation of propene and 1-butene, (ii) methanization of carbon dioxide, (iii) isomerization of 1-butene, (iv) dehydrogenation of cyclohexane, (v) conversion of equimolar mixture of CO and NO to CO_2 and N_2. Full conversions and 100% selectivities were obtained in reactions (i), (ii), (iv) and (v) and an equilibrium composition in the reaction (iii). These catalysts showed no pyrophoric activity on exposing to air even at Ni content as large as 50 wt%.

Chuan-gao *et al.* (2005) investigated influences of temperature and concentration of $(Bu_4N)Br$ on synthesis of $NiAl_2(OCH_2CH_3)(8-\gamma)(acac) \gamma$. The precursor of Nano-$NiAl_2O_4$ powder was prepared by electrochemistry dissolution of nickel and aluminum (electricity quantity 1:3) in ethanol and acetyl-acetone solution. $NiAl_2O_4$ were obtained by a direct sol-gel process under pH = 8.5 of the electrolyte solution, drying and calcinations for 2 h at the temperature of 350°C. IR spectrum, TG-DTA, XRD and TEM were applied to investigate the structures of the precursor and nano-sized $NiAl_2O_4$.

The experiments showed that the temperature controlled between 54°C-60°C, and the concentration of Bu_4NBr of 0.045 mol/l as conductive additive could improve current efficiency and electrolysis yield, and nano-sized $NiAl_2O_4$ with a narrow size distribution of 30nm can be obtained for 2 h at 350°C.