

Chapter 2

Literature Review

2.1 Ferrites

Ferrites are chemical compounds with the formula of AB_2O_4 , where A and B represent various metal cations, usually including iron. Ferrites are the well-known ferrimagnetic materials that consist mainly of ferrimagnetic oxides and, therefore, are electrically insulating. Ferrites are widely used in high-frequency applications, because an alternating current (AC) field does not induce undesirable eddy currents in an insulating material [16]. Ferrites are considered a class of spinels that consist of cubic, close-packed oxides with A cations occupying 1/8th of the octahedral voids and B cations occupying half of the octahedral voids. For an inverse spinel structure, half the B cations occupy tetrahedral sites, and both the A and B cations occupy the octahedral sites. Meanwhile, divalent, trivalent and quadrivalent cations can occupy the A and B sites, and they include Mg, Zn, Fe, Mn, Al, Cr, Ti and Si. Ferrites are usually non-conductive ferromagnetic ceramic compounds derived from iron oxides as well as oxides of other metals. Like most other ceramics, ferrites are hard and brittle. Ferrites are widely used in high-frequency applications because an AC field does not induce undesirable eddy currents in an insulating material. Based on the magnetic properties, ferrites are often classified as soft and hard ferrites as shown in Fig. 2.1.

2.1.1 Soft Ferrites

Soft ferrites are characterized by a small value of coercivity, so they cause low hysteresis loss at high frequency. They are widely used in electromagnetic cores of transformers, switching circuits in computers and radio-frequency (RF) inductors, e.g. lithium ferrite, nickel ferrite and manganese–zinc ferrite.

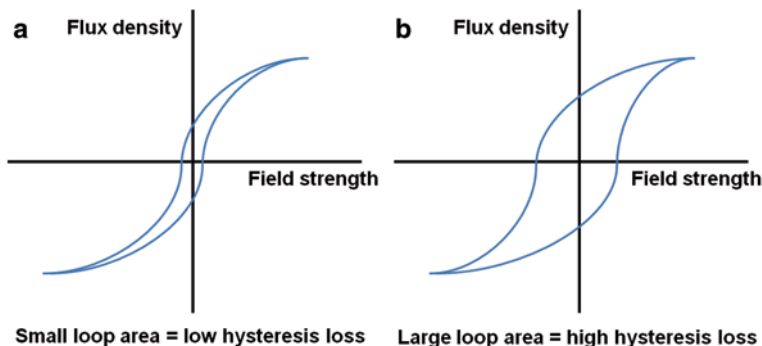


Fig. 2.1 Hysteresis loop for a soft and b hard ferrites

2.1.2 Hard Ferrites

Hard ferrites are characterized by a large value of retentivity and coercivity after magnetization, so they find applications as permanent magnets in radios, e.g. barium and strontium ferrite. The maximum magnetic field is about 0.35 (T) and the magnetic field strength is about 30–160 (kA/m). Ferrites are ferromagnetic materials that are typically oxides of mixed transition metals involving iron. For example, MnFe_2O_4 and Mg–Zn ferrite can form compounds of the formula $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. They are usually insulators in nature and, like most other ceramics, hard and brittle. In terms of the magnetic properties, ferrites are often classified as “soft” and “hard” which refers to their low or high coercivity of their magnetism, respectively. These ceramic materials are used in applications such as magnetic components in microelectronics. Most of the ferrite particles used to synthesize magnetic fluids are of the spinel structure. This structure consists of a cubic close-packed case of oxygen ions with the metallic ions occupying the tetrahedral A and octahedral B interstitial sites.

2.2 Structure of Unit Cell of Spinel Ferrite

The unit cell of spinel ferrites consists of 32 oxygen, 16 trivalent iron and 8 divalent metal ions. The most important feature of the unit cell is that its array of oxygen ions reveals two types of interstices, which can be filled by the metal ions. These interstices are referred to as tetrahedral or A sites and octahedral or B sites. Figure 2.2 shows the unit cell of the spinel structure.

There are two groups of four cubes (octants). The ionic positions are different in two octants sharing a face or a corner and the same in two octants sharing an edge. Thus, it is necessary only to show the positions of the ions in two adjacent octants.

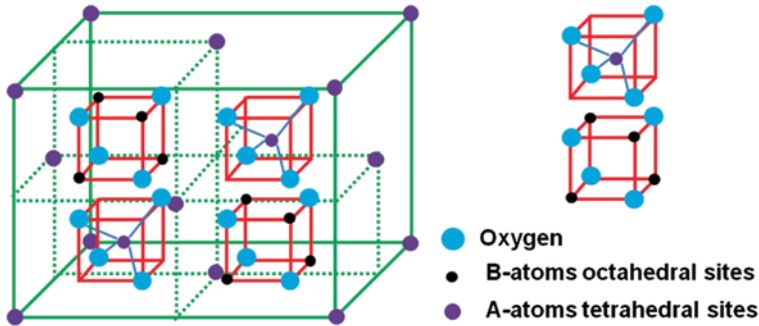


Fig. 2.2 The unit cell structure of spinel ferrite

Table 2.1 Metal ion arrangements in spinel ferrite unit cell with composition $(MO.Fe_2O_3)$

Types of interstitial site	Number available	Number occupied	Normal spinel	Inverse spinel
Octahedral	64	8	$8M^{2+}$	$8Fe^{3+}$
Tetrahedral	32	16	$16Fe^{3+}$	$8Fe^{3+} 8M^{2+}$

M metal ion

Note that each octant contains a central metal ion (small violet sphere) surrounded by the tetrahedral of oxygen ions. This ion is said to occupy an A site. The right-hand octant shows four metal ions (small black spheres) each surrounded by an octahedron (one of which is shown) formed by six oxygen ions. Such ions are said to occupy B sites. In a unit cell, there are 64 A sites, 8 of which are occupied, and 32 B sites, 16 of which are occupied.

The divalent metal ions commonly used in ferrites can be classified into those preferring B sites (Co, Fe, Ni) and those preferring A sites (Mn and Zn). In the normal spinel structure, the 8 divalent metal ions go into the A sites, and the 16 trivalent iron ions have preference for B sites. However, these 8 of 16 trivalent iron ions can sometimes transfer to the A sites by replacing the position of 8 divalent ions. This results in an inverted spinel as shown in Table 2.1 [17]. The two ionic species are distributed over the octahedral sites with some randomness.

The non-magnetic ions occupy eight B sites, whereas the iron is evenly divided between the two lattice sites. The AB interaction, overriding the AA and BB interactions, leads to a parallel arrangement within each sublattice. The net magnetization vanishes because the divalent ions have no magnetic moment.

The localization of ions in either the A or B sites depends fundamentally on the ion and lattice sizes, as well as the temperature and the orbital preference for specific coordination. In general, divalent ions are larger than trivalent ions (Table 2.2). The trivalent ion nuclei produce greater electrostatic attraction, hence their electron orbits contract. The octahedral sites are larger than the tetrahedral sites and, thus, the divalent ions are localized in the octahedral sites, whereas trivalent ions are in the tetrahedral sites [18].

Table 2.2 Radii of metal ions commonly involved in spinel ferrites

Ion	Ionic radius (Å)
Fe ²⁺	0.83
Fe ³⁺	0.67
Co ²⁺	0.82
Zn ²⁺	0.74
Ni ²⁺	0.78
Mn ³⁺	0.70

Table 2.3 Anisotropy constants of some ferrites [18]

Ferrite	Anisotropy constant K_1 (erg/cm ³)
FeFe ₂ O ₄	-1.1×10^3
Co _{0.8} Fe _{2.2} O ₄	3.9×10^6
MnFe ₂ O ₄	-28×10^3
Co _{0.3} Mn _{0.4} Fe ₂ O ₄	1.1×10^6

Ferrites have two different structural symmetries, determined by the size and charge of the metal ions, which balance the charge of the oxygen ions and their relative amounts [18].

2.2.1 Cobalt Ferrite

Some properties of ferrites can be enhanced by the incorporation of divalent metallic ions inside their structure. In the case of cobalt ferrite, the incorporation of cobalt ions results in an increase in coercivity due to an increased magnetocrystalline anisotropy resulting from the coupling of the spins of the cobalt and iron ions [19]. Cobalt ferrite (CoFe₂O₄) is a cubic ferrite with an inverse spinel structure where Co²⁺ ions are located in B sites and Fe³⁺ in the A and B sites. This ferrite is characterized by having an anisotropy constant higher than that of the common ferrites (Table 2.3) such as magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃). The anisotropy constant of bulk cobalt ferrite is in the range of $1.8\text{--}3.0 \times 10^6$ erg/cm³ and the saturation magnetization is 80.8 emu/g at room temperature and 93.9 emu/g at 5 K [20].

It has been observed that the magnitude of magnetic properties depends on the particle size. A decrease in particle size results in a decrease in coercivity and saturation magnetization, whereas the susceptibility and anisotropy constant have been reported to increase [21].

2.2.2 Hexagonal Ferrites

Hexagonal ferrites are widely used as permanent magnets and are characterized by possessing a high coercivity [22]. Their general formula is MO.6Fe₂O₃ where M can be Ba, Sr or Pb. The hexagonal ferrite lattice is similar to the spinel structure, with the oxygen ions closely packed, but some layers include metal ions, which have similar ionic radii as the oxygen ions. This lattice has three different sites occupied by metals: tetrahedral, octahedral and trigonal bi-pyramid.

2.3 Substitution in Ferrites

In the case of substituted ferrites materials, some of the ferric ions are replaced by trivalent ions of another metal. The effect on the magnetization depends on the site preferred by the substituent; e.g. aluminium prefers octahedral coordination and, therefore, reduces the magnetization of the substituted ferrite. It is not easy to predict the ion distribution in advance.

2.4 The Effect of Different Spinel Ferrite Phases on Their Properties

There is some possibility of getting the complex phases of final product from spinel ferrite synthesis. The previous research work reported that there are eight phases obtained from solution precursor plasma sprayed process which are: (a) Fe_3O_4 , (b) $\alpha\text{-FeOOH}$, (c) $\gamma\text{-Fe}_2\text{O}_3$, (d) $\alpha\text{-Fe}_2\text{O}_3$, (e) CoOOH , (f) Co_3O_4 , (g) CoO and (h) CoFe_2O_4 [23]. Each phase presents different ferromagnetic properties as described below.

G. H. Lee [24] observed unusual magnetic behaviours in the goethite composites. They found an additional phase transition near 12.5 K, a small, but sharp, drop near 12.5 K, and a slow decay with T for $13 < T < 220$ K in both the remanence (M_r) and coercivity (H_c). Haematite ($\alpha\text{-Fe}_2\text{O}_3$) presents low-temperature magnetic transition at 260 K (Morin temperature). The magnetic arrangement has Fe^{3+} spins directed along the (111) axis and paired across the shared octahedral face at $T \leq 260$ K. On the other hand, the spins become essentially localized in (111) sheets directed towards the three nearest neighbours at $T \geq 260$ K. However, the spins have canted slightly out of the plane, giving rise to a weak ferromagnetic moment along the (111) axis. Jong-Ryul Jeong et al. [25] performed the magnetization and magnetic hysteresis measurement of $\gamma\text{-Fe}_2\text{O}_3$ composites using a superconducting quantum interference device (SQUID) magnetometer from 5 to 300 K. The SQUID measurements revealed superparamagnetism of composites with the blocking temperature of 119.5 and 94.3 K for the composites made by the pipette drop method and the piezoelectric nozzle method, respectively. Sufi R. Ahmed et al. [26] discovered that diblock copolymer CoFe_2O_4 nanocomposites are superparamagnetic at room temperature and ferrimagnetic at 5 K. The magnetization of the nanocomposite remains unsaturated up to the highest field of 50 kOe. This is an indication of strong surface-spin pinning at the particle/support interface, resulting in a non-collinear spin structure within the CoFe_2O_4 particles. Myung Joon Han [27] found that the wurtzite (CoO) is a Mott insulator with antiferromagnetic spin ordering in its ground state, similar to the case of rock-salt CoO. This suggests that the wurtzite phase of CoO is not responsible for the observed magnetic signal from CoO nanocrystals. Finally, K. Parvin [28] studied the magnetization of Fe_3O_4 versus temperature in the temperature range 2.5–160 K, which was measured in zero-field-cooled and field-cooled experiments, while a blocking temperature (T_b) of 520 K was obtained. Above T_b ,

the nanoparticles show superparamagnetic behaviour and the magnetization versus field for various temperatures follows the Langevin function. $M-H$ curves below T_b indicate the ferromagnetic behaviour with $H_c = 560-400$ Oe for temperature $T = 2.5-18.5$ K.

Moreover, the different spinel ferrite phases also influence antibacterial property of nanocomposite. Sanpo et al. [29] found that nanopowders obtained from all citric acid (CA) systems and 15% polyvinyl alcohol (PVA) were pure spinel cobalt ferrite nanopowders. On the other hand, nanopowders synthesized from 5 and 10% of PVA presented some impurities in the form of haematite phases. The structural and morphological variants of the cobalt ferrite nanopowders manufactured from different chelating routes influence the *Escherichia coli* and *Staphylococcus aureus* survivor rate.

2.5 The Sol–Gel Method

Sol–gel processing has become a well-known method in the past few decades since it has been used in different research areas. Therefore, the aim of this following section is to provide an overview of the sol–gel process with respect to this specific work.

2.5.1 History

The study of sol–gel processing on inorganic ceramic and glass materials began in the mid-1800s by Graham [30]. These early investigators observed that the hydrolysis of tetraethyl orthosilicate under acidic conditions yielded SiO_2 in the form of a “glass-like material”. However, little technological interest was raised by these studies due to the long drying times required to obtain large monolithic pieces. The gels attracted the attention of chemists and researchers [31] in the late 1800s through to the 1920s. Despite the descriptive literature published about these studies, the understanding of physical–chemical properties of gels was limited. The second revival of the technique arose when the sol–gel method was employed by the ceramic industry in the 1950s and 1960s to synthesize a large number of novel ceramic oxide compositions (Al, Si, Ti and Zr, etc.) that were unavailable by traditional ceramic powder methods. The third boom came in the 1980s, when the sol–gel method was rediscovered by the micro-optical and heterogeneous catalytic industries. There are many factors that made sol–gel technology gain popularity, such as the versatility, excellent control over the properties of the material and very high and homogeneous component distribution. This phenomenon is indicated by the increase in the number of registered US patents using sol–gel elements, as depicted in Fig. 2.3. The registered US patents were collected by Google website patent searching.

The sol–gel method is employed in several industrial fields, such as optics [32], electronics [33], biotechnology [34], the drug industry [35] and heterogeneous ca-

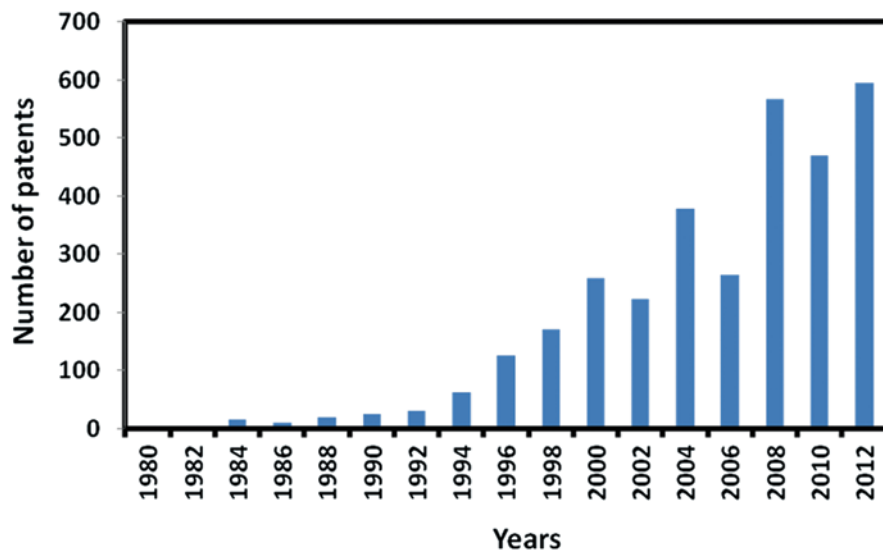


Fig. 2.3 Number of annually registered US patents related to the sol–gel method

talysis [36]. Sol–gel methods are finding novel applications that are based on the capacity of the technique to build complex, multicomponent systems in one single step.

2.5.2 The Sol–Gel Processing Method

Sol–gel processing is a chemical engineering technique to manufacture ceramic powders, especially oxides. The term *sol* refers to the initial solution of the chemical components from which the final powder will eventually be derived. *Gel* is a term used to describe the final product of the ceramic material. The methods are based on mixing solutions that enable reactions for the formation of distinct particles. It is important to note that the particles are not precipitated from solution; rather, the mechanism of particle production is based on colloidal science in which the particles are suspended in the liquid. Typical ceramic powders that are produced by this technique include chromia [37], alumina [38], cobalt ferrite [39] and ceramic alloys of stabilized zirconia [40].

The most widely used synthetic technique for bulk metal oxides has been the ceramic method, which is based on the direct reaction of powder mixtures. These reactions are completely controlled by the diffusion of the atomic or ionic species through the reactants and products. To bring the reaction partners sufficiently close together and to provide high mobility, these solid-state processes require high temperature and small particle sizes. Although the harsh reaction conditions only lead to thermodynamically stable phases, preventing the formation of metastable solids,

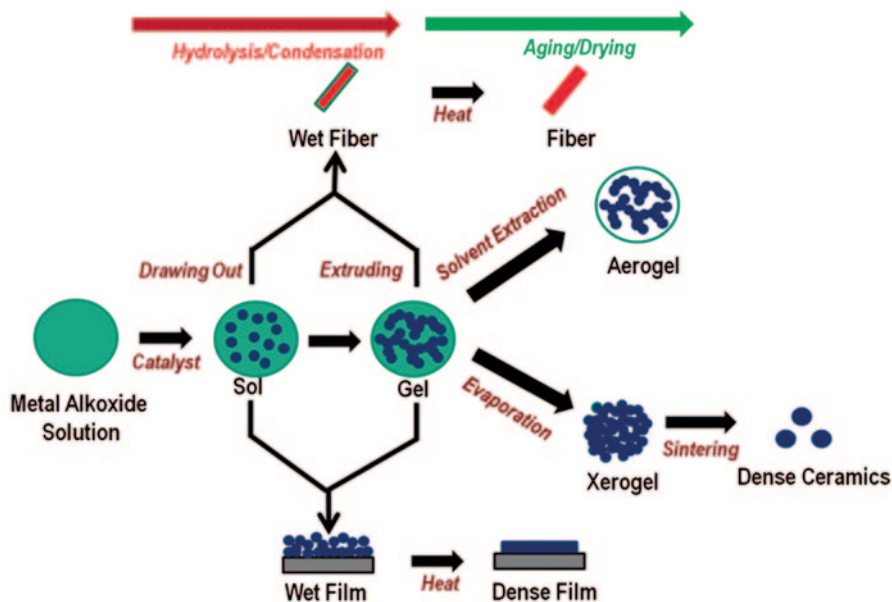


Fig. 2.4 Various steps in the sol–gel process to control the final morphology of the product [44]

these approaches gave access to a large number of new solid compounds, enabling the development of structure–property relationships. However, in comparison to organic chemistry, where highly sophisticated synthetic pathways are employed to make and break chemical bonds in a controlled way, the ceramic method is a rather crude approach. It is therefore no surprise that the size- and shape-controlled synthesis of nanoparticles especially liquid-phase routes represent the most promising alternatives. There are various products that can be collected from the sol–gel process (Fig. 2.4) and these depend on the synthesizing route.

Sol–gel procedures were successful in the preparation of bulk metal oxides (e.g. ceramics, glasses, films and fibres) [41] and, therefore, they have been applied for nanoparticle synthesis. Liquid-phase routes represent the most promising alternatives for the size- and shape-controlled synthesis of nanoparticles [42]. The number of oxide nanoparticles obtained by sol–gel chemistry is small compared to the variety of compounds obtained via powder routes [43].

It turned out that in many cases, a synthesis protocol developed for a bulk metal oxide could not directly be adapted to its corresponding counterpart on the nanoscale. The reasons for this observation are manifold. Aqueous sol–gel chemistry is quite complex, on the one hand due to the high reactivity of the metal oxide precursors towards water and the double role of water as ligand and solvent and, on the other hand, due to the large number of reaction parameters that have to be strictly controlled (hydrolysis and condensation rate of the metal oxide precursors, pH, temperature, method of mixing, rate of oxidation, the nature and concentration of anions) in order to provide good reproducibility of the synthesis protocol [45]. An-

other fundamental problem of aqueous sol–gel chemistry is that the as-synthesized precipitates are generally amorphous. The required post-synthetic annealing step to induce the crystallization process prevents any subtle control over crystal size and shape. For the preparation of bulk metal oxides, these limitations play only a minor role; however, in the case of nanoparticle synthesis, they constitute a major issue.

Nonaqueous (or nonhydrolytic) sol–gel processes in organic solvents, generally under exclusion of water, are able to overcome some of the major limitations of aqueous systems [46], and thus represent a powerful and versatile alternative. The advantages are a direct consequence of the role of the organic components in the reaction system that act as (1) a solvent, (2) an organic ligand of the precursor molecule, (3) a surfactant that enables chemical reaction or (4) a surfactant that permits the in situ formation of organic condensation products. On the one hand, they act as oxygen supplier for the oxide formation and strongly determine the particle size and shape as well as the surface properties due to their coordination properties, and on the other hand, the moderate reactivity of the oxygen carbon bond generally results in slower reaction rates. Nonaqueous synthesis routes generally yield metal oxide nanoparticles which present uniform nanostructure, complex crystal morphologies, and good dispersibility in organic solvent. Another important point is the fact that the chemistry of the oxygen–carbon bond is well known from organic chemistry. This aspect is of utmost significance considering the fundamental role of organic reaction pathways in nonaqueous sol–gel chemistry approaches. Parallel to the formation of the inorganic nanoparticles, also the initial organic species undergo transformation reactions often following elementary mechanisms of organic chemistry [47]. Based on the identification and quantification of these organic by-products, it is possible to correlate the processes leading to these organic species by retrosynthetic analysis to the growth mechanisms of the oxide nanoparticles.

2.5.3 *Aqueous Sol–Gel Chemistry*

The aqueous sol–gel process can be defined as the conversion of a precursor solution into an inorganic solid via inorganic polymerization reactions induced by water. In general, the precursor or starting compound is either: (1) an inorganic (i.e. no carbon), (2) a metal salt (chloride, nitrate, sulfate), or (3) a metal organic compound, such as an alkoxide. Metal alkoxides are the most widely used precursors in wet chemical synthesis because they react readily with water and can be found in several form of metals. Some alkoxides, which are widely used in industry, are commercially available at low cost (e.g. Si, Ti, Al, Zr), whereas others are rarely available or costly (e.g. Mn, Fe, Co, Ni, Cu, Y, Nb, Ta).

The first step in an aqueous sol–gel reaction is the formation of an inorganic polymer by hydrolysis and condensation reactions, i.e. the transformation of the molecular precursor into a highly cross-linked solid. Hydrolysis leads to a sol, a dispersion of colloidal particles in a liquid, and further condensation results in a gel, an interconnected, rigid and porous inorganic network enclosing a continuous liquid phase. This transformation is called the sol–gel transition. There are two

possibilities to dry the gels. Upon removal of the pore liquid under hypercritical conditions, the network does not collapse and aerogels are produced. When the gel is dried under ambient conditions, shrinkage of the pores occurs, yielding a xerogel. One of the highly attractive features of the sol–gel process is the possibility to shape the material into any desired form such as monoliths, films, fibres and monosized powders, and subsequently to convert it into a ceramic material by heat treatment.

As mentioned before, the sol–gel processes can be classified into two different routes depending on the nature of the precursors: (a) the precursor is an aqueous solution of an inorganic salt or (b) a metal organic compound [48]. The inorganic route involves the formation of condensed species from aqueous solutions of inorganic salts by adjusting the pH, by increasing the temperature or by changing the oxidation state. But this method has several disadvantages. The aqueous chemistry of transition metal ions can be rather complicated because of the formation of a large number of oligomeric species, depending on the oxidation state, the pH or the concentration.

The role of the counter anions, which are able to coordinate the metal ion giving rise to a new molecular precursor with different chemical reactivity towards hydrolysis and condensation, is difficult to predict. These ions can influence the morphology, the structure and the chemical composition of the resulting solid phase. Also, the removal of these anions from the final metal oxide product is often a problem. Many of these issues can be avoided by using metal alkoxides as precursors. They are often soluble in organic solvents, providing high homogeneity, and they can easily be converted to the corresponding oxide. The sol–gel conversion of metal alkoxides involves two main reaction types: hydrolysis and condensation (Fig. 2.5).

During hydrolysis, the alkoxide groups ($-OR$) are replaced via the nucleophilic attack of the oxygen atom of a water molecule under release of alcohol and the formation of a metal hydroxide. Condensation reactions between two hydroxylated metal species leads to $M-O-M$ bonds under release of water (oxolation), whereas the reaction between a hydroxide and an alkoxide leads to $M-O-M$ bonds under release of an alcohol (alkoxolation). Chemical aspects play an important role in controlling the sol–gel process. The chemical reactivity of metal alkoxides towards hydrolysis and condensation depends mainly on the electronegativity of the metal atom, its ability to increase the coordination number, the steric hindrance of the alkoxy group and the molecular structure of the metal alkoxides (monomeric or oligomeric). The amount of added water in the hydrolysis step and how the water is added determine whether the alkoxides are completely hydrolysed or not and which oligomeric intermediate species are formed. Additional parameters are the polarity, the dipole moment and the solvent's acidity.

The major challenge of sol–gel methods, especially for those methods based on the hydrolysis and condensation of molecular precursors, is control over the reaction rates. For most transition metal oxide precursors, these reactions are too fast, resulting in loss of morphological and structural control over the final oxide material. Moreover, the metal alkoxides exhibit a range of reactivities that make it difficult to control the composition and the homogeneity of complex multi-metal oxides formed via the sol–gel process. The reactivity of the precursors can be altered by



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