INVITED PAPER: FUNDAMENTALS OF SOL-GEL AND HYBRID MATERIALS PROCESSING

Molecular mechanisms of the metal oxide sol-gel process and their application in approaches to thermodynamically challenging complex oxide materials

Vadim G. Kessler [1] · Gulaim A. Seisenbaeva[1]

Abstract
This review presents a brief overview of recent insights into general reaction pathways in sol-gel synthesis of metal oxides. Metal-based sol-gel precursors display kinetically unhindered reactivity, combining high reaction speed with reversibility on a molecular level. The process producing metal oxide sols can thus be described as nucleation of an oxide phase with growth option efficiently precluded by extremely low solubility. The emerging nuclei are essentially Polyoxometalate (POM) species, with sizes in the colloid range starting from about 2 nm. They are stabilized in solution by colloid forces (charge interactions, hydrogen bonding, van der Waals forces), defined by the nature and arrangement of species on their surface, which permits them to be denoted as Micelles Templated by Self-Assembly of Ligands (MTSALs). The sol-gel transition occurs on aggregation of particles resulting in percolation. Exploiting this mechanism, it is possible to produce materials with controlled porosity, biocompatibility, and even to access thermodynamically challenging phases that cannot be produced by conventional synthetic techniques.

Graphical Abstract
Metal oxide Sol-Gel can be described as nucleation of an oxide phase resulting from one-step coordination equilibrium in solution, followed by aggregation without growth.
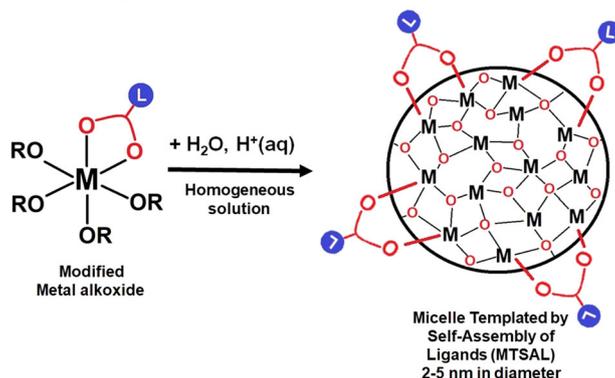
Keywords Thermodynamic control · Coordination equilibrium · MTSAL · Paperbag compounds · Complex oxides

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Highlights

- Metal alkoxides are strong Brönsted and Lewis bases, undergoing hydrolysis via proton-assisted S_N1 mechanism
- Hydrolysis and polycondensation are for metal alkoxides a single kinetic phenomenon, leading to nucleation of an oxide phase
- The metal oxide nuclei are colloid particles 2–5 nm in size with Polyoxometalate structure—a well-ordered core in a shell of ligands, permitting to describe them as Micelles Templated by Self-Assembly of ligands

1 Introduction

Sol-gel technology from its very first steps has attracted the strong attention of materials chemists, due to its versatility in approach to materials possessing rather varied physical shape and morphology. Discovered originally for silica [1], it received already early in its history a number of spectacular applications involving metal oxides. Among those, it is important to mention the approach to mesoporous alumina developed in the dissertation of Vyacheslav Tishchenko in 1898 [2] and the T-Star technology for antireflective coatings, involving thin TiO_2 layers, invented by Alexander Smakula at Carl Zeiss in the 1930s [3].

Controlled synthesis of materials with different structural, morphological, and, not the least, chemical characteristics, requires understanding of the nature of processes, guiding their formation. The eagle-eye overview of Sol-Gel materials chemistry is given usually in the way presented in Fig. 1, rooted, quite probably, in the illustrative materials to the lectures of Alexander Smakula at MIT in the 1950s. In this description, the precursor is a metal alkoxide solution, transformed into what appears to be uniform spherical particles in a colloid solution (sol). The latter undergo further aggregation and densification to yield different kinds of functional shapes and morphologies—uniform dense coatings by deposition on a substrate, xerogels on air-drying, and, via further thermal treatment, dense ceramics, uniform nanoparticles via controlled precipitation, aerogels via solvent replacement, wires by dragging a thread that is then subjected to annealing, etc.

In the old courses in sol-gel technology, a common comment on this graphic overview, when moving to description of the chemical mechanisms, was: "Let's look at the reactions of a metal alkoxide, for example, silicon alkoxide". This was apparently a very controversial move, because silicon, as Inorganic Chemistry clearly states [4], is not a metal, but a metalloid, i.e., a non-metal element with low electronegativity, possessing dense simple substance forms with semiconductor properties. It is, however, a good starting point for discussion of Sol-Gel mechanisms, to focus first on the molecular chemistry and reactions of silicon derivatives.

Fig. 1 Overview of the Sol-Gel approaches to different classes of materials [https://en.wikipedia.org/wiki/Sol%E2%80%93gel_process]
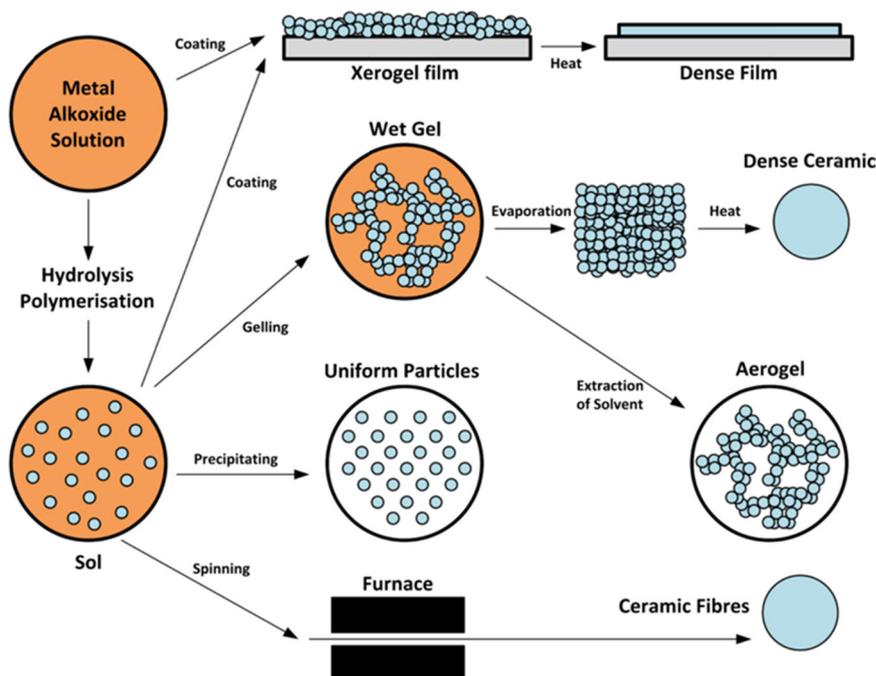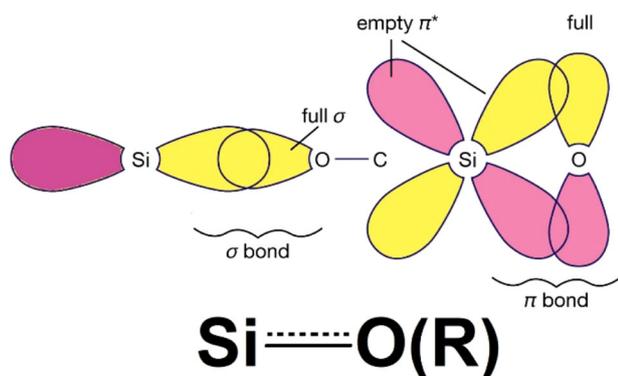
Fig. 2 Ester character of the Si-OR bond explained via atomic orbital interactions (based on Encyclopedia Britannica explanation [https://www.britannica.com/science/coordination-compound/Ligand-field-and-molecular-orbital-theories])

2 Sol-gel chemistry of silica

The nature of element-oxygen bonding in the compounds of silicon is predominantly covalent, rendering relatively slow reaction rates for compounds involving these bonds, which, in particular is responsible for weathering stability of polymeric silicates, feldspars and clays, in nature [5]. The silicon-oxygen bond is weakly polar and displays a pronounced ester character due to interaction of the filled p-orbitals of oxygen atoms and vacant d-orbitals of the silicon ones, the pπ-dπ donor-acceptor mechanism (see Fig. 2).

This mildly polar Si-O bonding is responsible for the poor solubility of silicon alkoxides in water and their considerable resistance to hydrolysis in the absence of catalysts. It usually requires addition of a less polar solvent such as alcohol or THF to ensure dissolution of silicon alkoxides. Kinetic characteristics of the hydrolysis process for alkoxysilanes resemble those of the carboxylic esters: larger size of the alkyl group is associated with a slower hydrolytic transformation. The hydrolysis rate varies in the series: R = Me > Et > nPr > iPr ≈ nBu [6].

The effects of acidic and basic catalysis of hydrolysis have been explained in a very illustrative way in the works of Brinker and Scherrer [7–9]. In the basic medium, the reaction of hydrolysis proceeds according to the addition-elimination mechanism often compared to the S_N2 type process (see Fig. 3a). As catalysts, either an alkali (usually sodium) hydroxide or ammonia, or even ammonium fluoride, can be used. The reaction is quite slow, being associated with a need to increase the coordination number of the silicon atom. It is worth noting that the product of hydrolysis is a siloxide anion, a considerably bulkier and weaker nucleophile compared to a hydroxide anion, which hinders its further condensation.

In the acidic medium, the reaction of hydrolysis proceeds much quicker because no increase in coordination number

is required in the S_N1 reaction. The forming alcohol is a good leaving group. The forming alkoxy-silicic acid has pronounced acidic properties in the alcohol solution, which promotes its further reaction with unhydrolyzed alkoxysilane species.

These well-established kinetic features led to important observations concerning the possibility to control the morphology and porosity of silica for cases when the reactions are carried out in alcohol media with addition of only small catalytic amounts of an acid or a base. For acidic catalysis, the speed of condensation in such conditions exceeds the speed of hydrolysis, resulting in wire-like morphology with low degree of cross-linking (see Fig. 4), while for basic catalysis the hydrolysis occurs quicker and is followed by slower condensation, resulting in highly cross-linked clusters (Fig. 4). The formation of linear spaghetti-like chains under acidic catalysis can be related to the lower electron donating effect of OSi groups with respect to OEt. This means that the partially positively charged Si are more favored in the terminal positions of a chain (more OEt groups, a single OSi group), vs the internal positions of the chain (2 OSi groups, 2 OEt groups). Similarly, the partially negatively charged pentacoordinated Si groups under basic catalysis are more favored at the centers of the chains, producing ramifications, with respect to the terminal Si atoms. The condensation kinetics could be followed by ^{29}Si NMR, confirming this hypothesis for such systems [10].

It is very important to mention that in predominantly aqueous medium in the presence of an excess of acid or base, the processes occur in a very different way. In strong acidic medium the hydrolysis is quick, resulting in supposedly partly protonated $Si(OH)_4$ that undergoes rather slow condensation according to in situ FTIR investigations [11]. This enables acidic conditions to be used very efficiently for production of mesoporous silica. In this process the free silicic acid slowly condenses around the surfactant micelles, forming a 3D ordered hexagonal or cubic structure of pores. In the strongly basic medium, the initially quick hydrolysis and polycondensation result in formation of in-principle nuclei of amorphous silica that then slowly grow, forming nano and then macro size spherical particles—the so-called Stöber process. The size of the resulting particles can be tuned rather finely via choice of precursor concentration, and basicity and salinity of the solution as factors influencing the colloid stability of the growing particles (see Fig. 5) as described originally by Iler [12]. Many recipes are available, describing conditions offering rather uniform particles with exact desired size (see, for example, [13]). The Stöber particles can grow around seeding particles or incorporate molecules present in solution. When they are produced in strongly basic medium (pH > 10) they become quite dense, excluding even microporosity that would be an

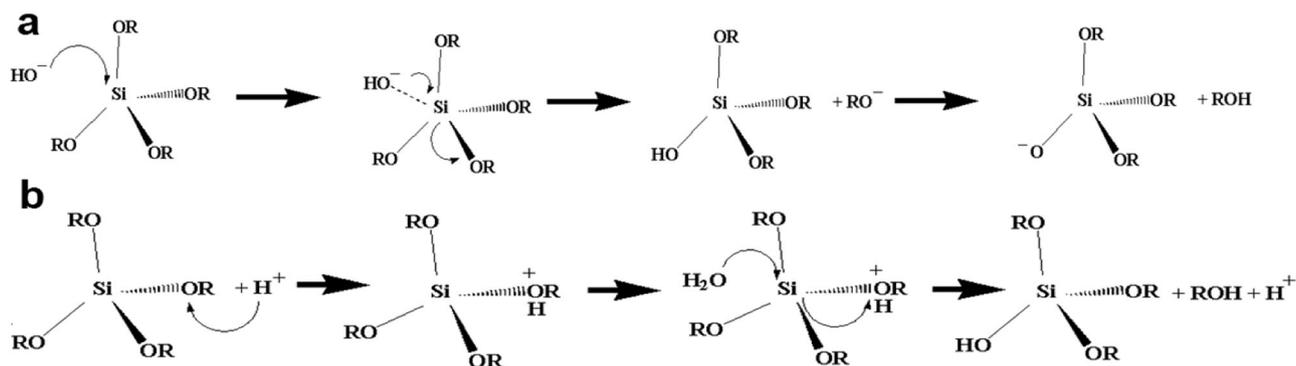Fig. 3 Hydrolysis pathways for alkoxy-silanes: basic catalysis via addition-elimination mechanism often described as S_N2 mechanism (**a**) and acidic catalysis via proton-assisted S_N1 mechanism, where the process starts with an electrophilic addition of the proton (**b**)
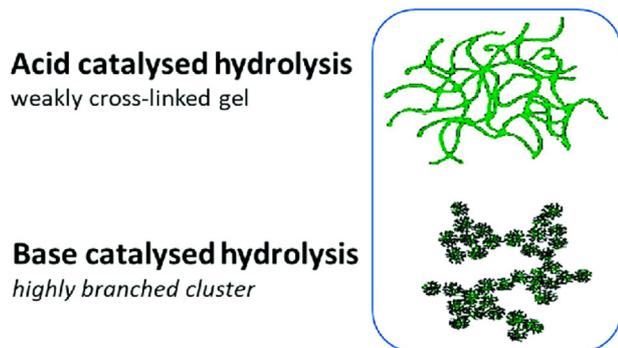

Fig. 4 Typical morphologies of polymeric gels produced in alcohol media with lower content of the catalyst. Reproduced with permission from [55]
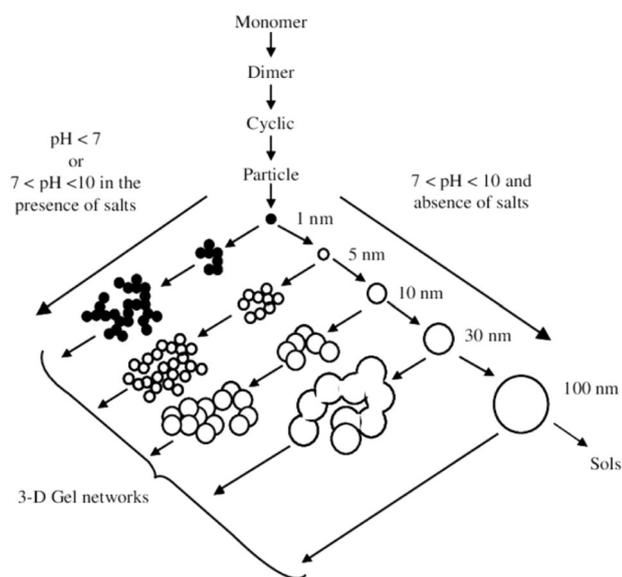

Fig. 5 Influence of pH and salinity on formation of silica in predominantly aqueous medium. Reproduced with permission from [56]

inherent property of polymeric particles. With a Stöber silica layer with thickness of 20 nm and higher it is possible to protect against dissolution and oxidation, for example, a magnetic iron oxide even in contact with concentrated nitric acid [14].

A special mention should be made regarding the effect on silicon alkoxides, the alkoxy-silanes, produced by introduction of chelating ligands. In contrast to the derivatives of aliphatic alcohols, the heteroleptic Si complexes with chelating ligands are highly humidity sensitive and hydrolyze without need of catalysts on contact with water in solution or from the atmosphere [15]. This is caused apparently by a combination of several factors (see Fig. 6). Introduction of a chelating ligand breaks the symmetry of bonding, decreasing its multiplicity (the "ester" character), contributes to increased charge distribution, which in turn renders the alkoxide oxygen more strongly negatively charged and thus more basic. The acidity of water molecules then becomes sufficient to protonate the alkoxide residue and cause its hydrolytic removal. Applying biocompatible polyols such as, for example, glycerol as chelating ligand, it is possible to design fully biocompatible ways to synthesize porous silica for use in separation of biomolecules [16, 17].

3 Structure, bonding and reactivity of metal alkoxides

The chemical nature of metal alkoxides is drastically different from that of alkoxy-silanes, the silicic acid esters. Theoretical calculations, even for highly charged +5 and +6 cations, reveal localization of occupied bonding molecular orbitals essentially solely on oxygen atoms of the alkoxide ligands [18, 19]. This means that these species are built by simple electrostatic, i.e., ionic bonding, associated in reactivity with quick and reversible ligand exchange reactions. Formation of heterometallic species for metal alkoxides has been broadly proved to be a result of coordination equilibria in solutions as demonstrated by reproducible solubility isotherms in complex systems (Fig. 7) [20].

Fig. 6 Preparation of heteroleptic silicon alkoxides incorporating chelating ligands (reproduced with permission from [15]) (**a**) and the effect of chelating ligand on the nature of Si-O(R) bonding (**b**)
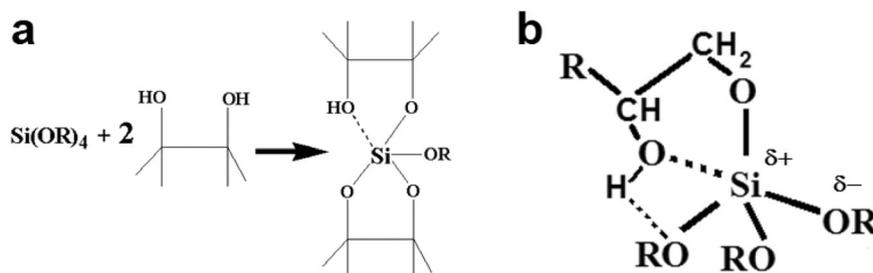
Fig. 7 Solution equilibria revealed by solubility isotherms in complex systems, involving two metal alkoxides and the parent alcohol as solvent. Reprinted with permission from [20]
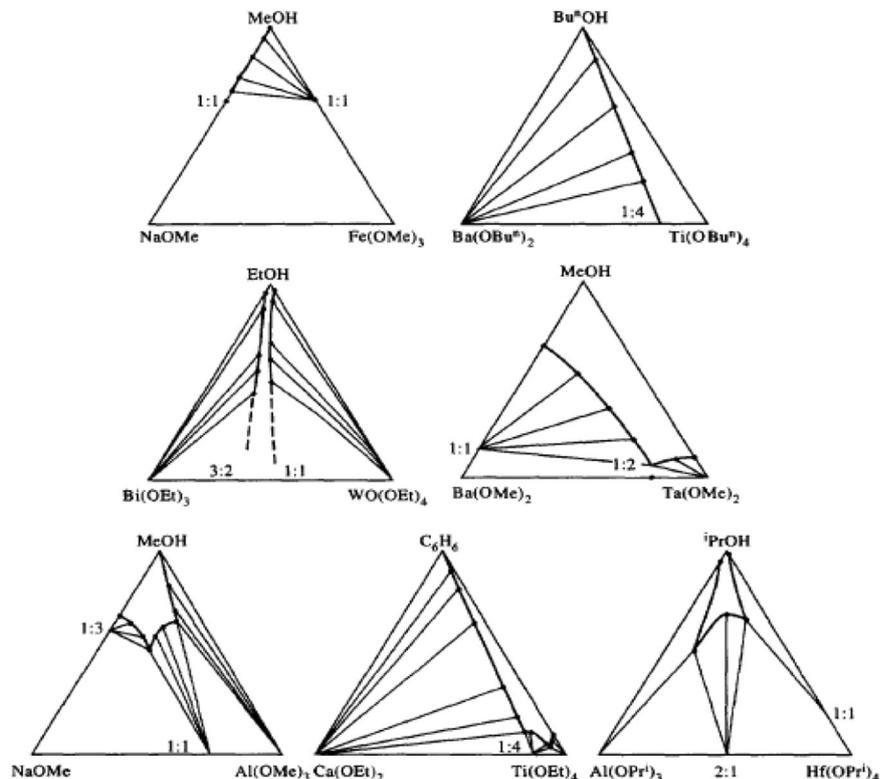
Fig. 7. Solubility isotherms in M(OR)$_x$–M'(OR)$_x$–L systems at 20 C (wt %).

It is important to note that the molecular structures of complex alkoxide species follow the Goldschmidt's principles of minimal radius ratios as principal factors determining their construction. Selecting a structure type for a desired chemical composition enables new heterometallic complexes to be constructed by compensating the charge and coordination requirements of cations via choice of ligands, providing the necessary number of donor atoms and possessing the needed size (volume angle requirements), see Fig. 8 [21]. The same type of structure can be built up, using cations with different charges by replacing pairs of simple alkoxide ligands with a chelating ligand with comparable angular size. For example, two ethoxide ligands are equivalent to one acetylacetonate (acac) ligand and two iso-propoxide ligands—to a 2,2,6,6-tetramethyl-heptane-dione-3,5 (THD) ligand. The same M_3X_{12} structure can be

Possibility to design structures of complex precursors

$$\sum_i \varphi_i \approx 4\pi$$
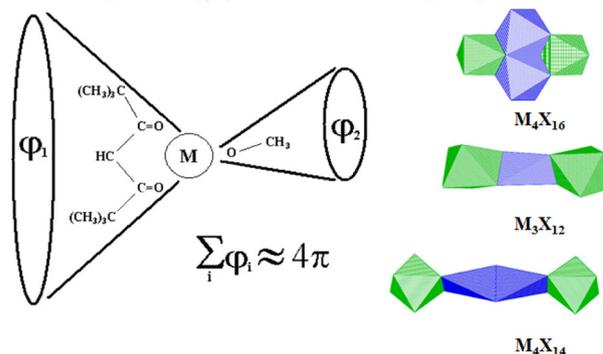
M_4X_{16}

M_3X_{12}

M_4X_{14}

Fig. 8 Molecular design approach to complex alkoxide structures, underlining the combinations of coordination polyhedrons as structural types serving as the basis for selection of ligands [21]

obtained with $M^{II}M^V_2(OR)_{12}$, $M^{II}M^{IV}_2(OR)_8(acac)_2$ and $M^{II}Al_2(OR)_4(acac)_4$ compositions, where OR are aliphatic alkoxide ligands.

It is important to mention that the chelating ligands are not remaining "glued" to the atom they were attached to initially, but jump between species in solution equilibria [22, 23]. Introduction of chelating ligands, just as for silicon derivatives and independently of their nature (polyols, beta-diketonates, carboxylates), increases the charge distribution in the molecules and kinetically facilitates hydrolysis [24, 25]. These ligands, however, can provide some thermodynamic stabilization against moisture, especially for a compound in the form of large crystals [21].

An important principal property of metal alkoxides is that they are functioning as both rather strong Brönsted and Lewis bases. Brönsted basicity is very apparent, because the alkoxide ligand is a conjugate base of the commonly used solvent, which is the parent alcohol. It must be noted that water is a much stronger acid than alcohols and water molecules interact with the alkoxide anions by protonating them, causing an electrophilic addition of a proton opening way for nucleophilic substitution i.e., initiating what has been described as proton-assisted S_N1 type substitution reaction. Lewis basicity is also due to the presence of an alkoxide ligand, bearing a free electron pair in the form of a bonding sigma-orbital located at the oxygen atom. Lewis basicity explains the often-observed aggregation of metal alkoxides, forming oligonuclear complexes, and even complex formation with alcohols (solvation) and with partially substituted amines. It is important to mention that when the additional donor molecules are not able to form a supporting hydrogen bond to the Lewis basic alkoxide ligand, no complexation is observed [26, 27]. Metal alkoxides are broadly used as basic catalysts [28, 29] in contrast to metal halides that are broadly applied as Lewis acids in synthetic organic chemistry, in particular, in electrophilic substitution reactions such as alkylation of aromatic rings [30].

4 Sol-gel chemistry of metal oxides

In the dawn of Sol-Gel chemistry, in the end of the 1980s to the beginning of the 1990s, when both molecular and materials characterization tools were scarce and not truly informative, the observation of quick transformation of precursors into metal oxides in organic media with only reaction with water, led to the erroneous assumption that metal oxide Sol-Gel chemistry could be controlled by homogeneous kinetics of hydrolysis-polycondensation and result in polymeric colloids [31]. The inspiration was taken from reactions of silica precursors in organic media with minor amounts of catalysts. Experimentally observed behavior with mass-precipitation of

hydrated oxide on addition of water was interpreted as formation of a highly cross-linked extended polymer. The observed delay of gelation on addition of chelating ligands was viewed as decreasing the speed of hydrolysis and condensation (without any direct kinetic evidence for the molecular mechanisms). It was suggested that addition of larger quantities of chelating ligands (dependent on the case, but usually over 2 equivalents per metal center) would results in stable molecular species ("clusters"), while intermediate substitution ratios would lead to branched polymers believed to offer a high degree of microporosity [32].

Subsequent studies of the Sol-Gel process revealed, however, a very different mechanism. It was demonstrated that the hydrolysis and condensation reactions are both quick and reversible and constitute a single kinetic phenomenon. Their products are species whose structures are defined not by step-by-step ligand substitution, but by straightforward coordination equilibrium. At low hydrolysis ratios, the structures of the formed species can easily be related to dense packing motifs and often mimic the forms observed for polyoxometalate (POM) species in aqueous media (see Fig. 9) [33].

Tracing this transformation pathway to a logical limit, it was proposed that in the presence of enough water (high hydrolysis ratios usually applied in Sol-Gel technology), the result of the process is a POM-like structure with a dense and well-ordered metal oxide core and ligand-covered shell, referred to as Micelle Templated by Self-Assembly of Ligands (MTSAL), underlying its colloid nature [33, 34] (see Fig. 10).

These structures act as nuclei of the final oxide phase. Sol-Gel can thus be seen as nucleation followed only by aggregation without growth. During the last two decades, this mechanism has received a multitude of convincing confirmations. Formation of chemically individual MTSAL particles was experimentally observed in hydrolytic transformation of homoleptic titanium and titanium/zirconium alkoxides using in situ DLS measurements [35, 36]. The size of the species remained the same in a broad interval of hydrolysis ratios with standard deviation 0.08–0.13 nm, a value not permitting any substantial variation in the chemical composition and indicative of the individual "molecular" nature of the species (see Fig. 11).

It was shown that gels of hydrated TiO_2 [37] and Nb_2O_5/Ta_2O_5 [38], produced by different routes, are built up by aggregation of MTSAL core-shell particles. Precipitates from hydrolysis of titanium alkoxides were peptized by nitric acid, transforming back to sols [39]. Crystalline TiO_2 material, consisting of uniform particles with a size below 10 nm, could be produced by hydrolysis of titanium alkoxides in boiling water [40]. Titania MTSALs were found to be generated in room-temperature ligand exchange equilibrium involving ammonium oxo-

Fig. 9 Illustration of the one-step transformations by hydrolysis-polycondensation on microhydrolysis: a tetramolybdate type molecule on addition of 1 equivalent of water in toluene/alcohol medium transforms quantitatively into a Lindquist type structure [33]
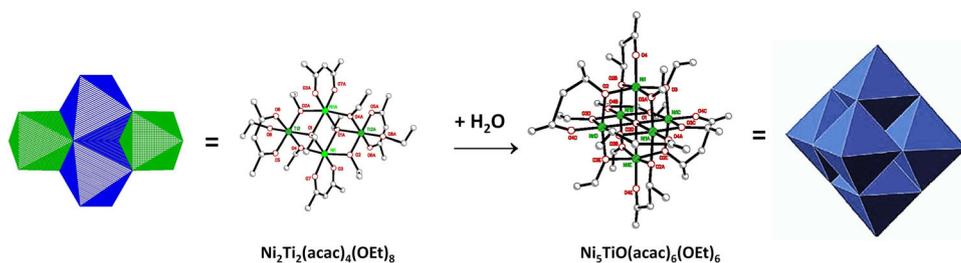
$Ni_2Ti_2(acac)_4(OEt)_8$ $+ H_2O$ $Ni_5TiO(acac)_6(OEt)_6$

Fig. 10 Sol-Gel mechanism in homogeneous medium leading to one-step formation of a MTSAL particle—a nucleus of an oxide phase, and in a double phase system—to coalescence of MTSALs at an interface, creating a continuous layer
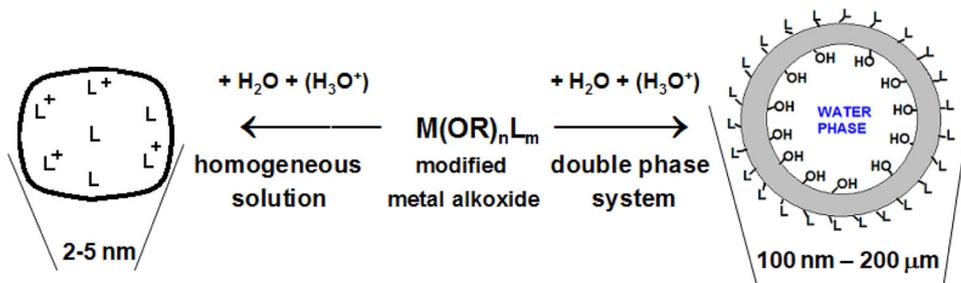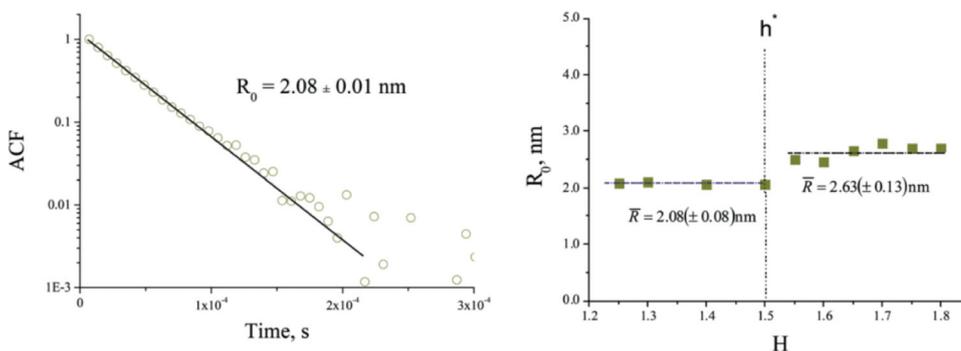
$+ H_2O + (H_3O^+)$ homogeneous solution ← $M(OR)_nL_m$ modified metal alkoxide → $+ H_2O + (H_3O^+)$ double phase system

WATER PHASE

2-5 nm   100 nm – 200 μm

Fig. 11 Auto-correlation function (ACF) vs time (left) and particle size vs hydrolysis ratio (right) for hydrolytic Sol-Gel synthesis of titania-zirconia powder. Reprinted with permission from [35]

$R_0 = 2.08 \pm 0.01$ nm

h^* $\bar{R} = 2.63(\pm 0.13)$nm $\bar{R} = 2.08(\pm 0.08)$nm

lactato-titanate with the commercial name TiBALDH [41]. Cassiterite structured crystalline SnO_2 MTSALs were formed by room temperature sol-gel transformation of $Sn(OtBu)_4$ in aqueous medium [42].

It was also demonstrated that oligonuclear oxo-alkoxide complexes of, in the first case, titanium, but even a number of other early transition elements, were not behaving as clusters, but, on the contrary, were prone to react further with the excess of water, especially in the presence of acids or salts, transforming into larger MTSAL species—nuclei of the corresponding oxide phases [43–45], see Fig. 12.

Cluster is a linguistically very distinct term used correctly for a structure containing metal-metal bonds. It is borrowed from the name of plant fruit structures with strong internal connections, such as clusters of grapes or clusters of wheat. Oxo-alkoxide complexes do not feature any stronger intrinsic bonding between metal atoms, resulting instead from self-assembly under the action of external forces. They resemble thus paper bags, used now in Europe for selling vegetables, filled with, for example, potatoes. We thus proposed to call such aggregates paper bags (see Fig. 13) in a recently published viewpoint article [46].

5 Approaching thermodynamically challenging materials—Single source precursor approach

The insight into the molecular mechanisms of the Sol-Gel process on the way to materials facilitates an explanation of the challenges that emerge on the way to utilizing single-source precursors of chemically complex materials. It is, unfortunately, insufficient to produce individual molecules incorporating different desired cations in a correct ratio. Such species are not clusters and can change completely with respect to both composition and structure on further hydrolytic transformation [47, 48]. This is just one of the challenges on this track. Another obstacle to cope with is that the desired oxide phase must exist under the conditions of precursor transformation into final material. If both conditions are fulfilled, which quite often is the case of complex oxides with 1:1 metal ratio and perovskite structure (as, for example, in the case of $BaTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ [49], where $M(II)TiO(OR)_4$ stable precursors form with secondary or even long-chain primary alkoxide residues R, or in case of REE doped $YAlO_3$ or $LaAlO_3$ [50], where alkoxide bridged

Fig. 12 Transformation of the oxo-alkoxide oligonuclear complexes (**a**) via intermediate ordered state (**b** and below, left) into oxide nanoparticles (MTSALs, **c** and below, right) [40, 43]
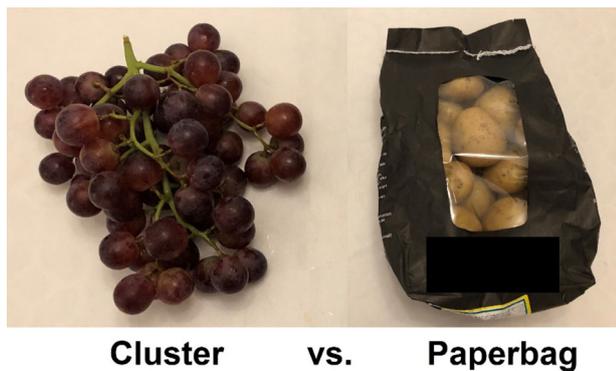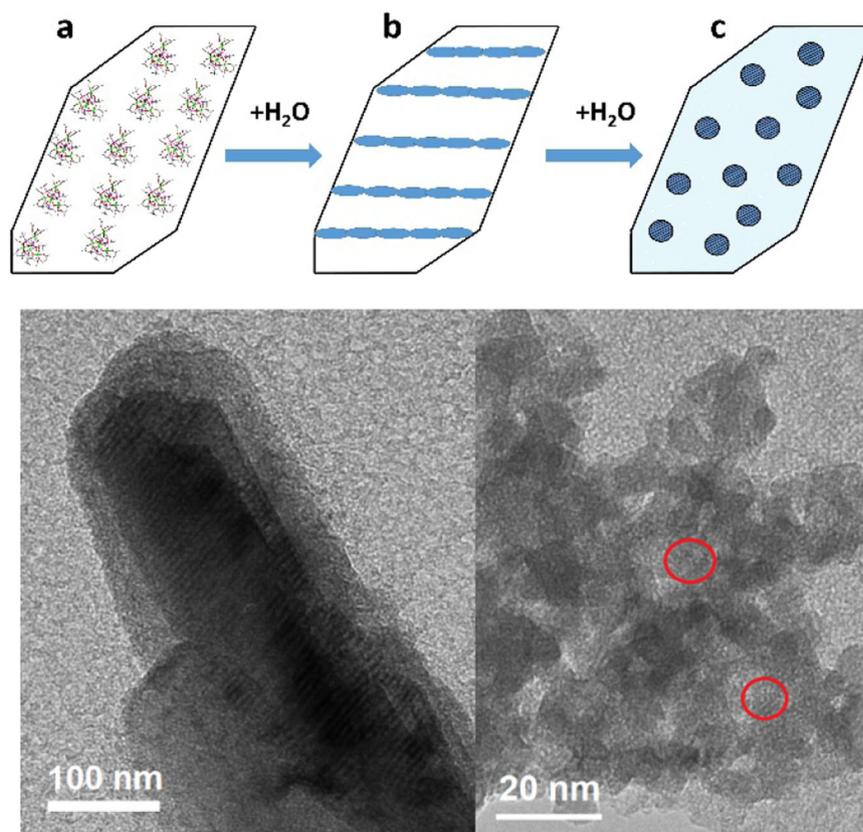

Fig. 13 Visual explanation for terminology describing different types of oligonuclear complex species—a cluster of grapes for molecules with metal-metal bonds, and a paper bag with potatoes for aggregates supported by external molecular self-assembly forces. Reprinted with permission from [46]
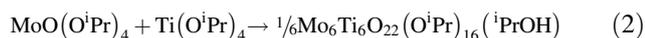
precursors are formed with sec-alcohols), the use of single-source precursor/intermediate may be reasonable.

When the desired phase does not exist under mild conditions, which is the case of, for example, High Temperature Superconductors, the single-source precursor approach in Sol-Gel is useless. In this review we will demonstrate that in the opposite situation, when the desired phase is (meta) stable, but the precursor is changing its composition, there

is still an option for use of a single-source precursor. In our recent studies, we have addressed two cases—one dealing with an almost mythological titanium molybdate phase TiMoO$_5$, expected to combine high anodic capacity for use in alkali metal batteries with particular thermal stability [51], and REE-doped TiO$_2$ for visible light photocatalysis [52]. The solution in both cases involved the initial isolation of a solid heterometallic compound with required composition, produced by microhydrolysis, and then subjected it to thermal decomposition under mild conditions (max 500 °C). The thermal decomposition might appear a high-energy technique, but when the process occurs entirely in the solid state, diffusion is limited and the energy is used mostly to improve crystallization of the oxide phase without separation of the components.

The challenge of titanium molybdate lies in the significant differences in the properties of homometallic oxides—refractory TiO$_2$ and volatile acidic MoO$_3$, which eliminates the possibility of producing the heterometallic oxide by conventional (or even high-pressure) solid state synthesis. Thus, a quest for a single-source precursor was justified. Producing a heteroelement compound was a challenge in itself with both cations being highly charged, excluding the usual Lewis acid-base reaction. It was apparent that an oxo-substituted species had to be produced. In the initial attempts, we applied a solution

thermolysis approach followed by re-oxidation that proved efficient in approaching Mo-Ta heterometallic precursors [53, 54]:

$$MoO(OMe)_4 + Ti(O^iPr)_4 \rightarrow \tfrac{1}{2}Mo_2Ti_2O_4(OMe)_6(O^iPr)_6 \quad (1)$$

$$MoO(O^iPr)_4 + Ti(O^iPr)_4 \rightarrow \tfrac{1}{6}Mo_6Ti_6O_{22}(O^iPr)_{16}(^iPrOH) \quad (2)$$

The yields was, however, quite low, presumably due to formation of a variety of byproducts. Applying a hydrolytic route (adding the stoichiometric amounts of water) to access the iso-propoxide complex, resulted in a very high yield in a slightly different structure, but still with approximately 1:1 metal composition:

$$MoO(O^iPr)_4 + Ti(O^iPr)_4 + 2.67\,H_2O(^iPrOH) \rightarrow \tfrac{1}{7}Mo_7Ti_{7+x}O_{31+x}(O^iPr)_{8+2x} \quad (3)$$
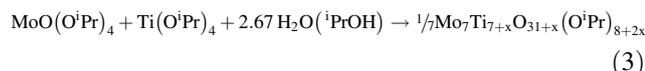
Using compound **3** for further production of TiMoO$_5$ by Sol-Gel failed, yielding MoO$_3$ as major crystalline reaction product after annealing at 500 °C. This indicated separation of components at higher hydrolysis ratios. On the contrary, metal-organic decomposition of Mo$_7$Ti$_{7+x}$O$_{31+x}$(O^{i}Pr)$_{8+2x}$ (3) produced single-phase TiMoO$_5$ with the expected structure (combination of TiO$_6$-octahedra, sharing corners with MoO$_4$-tetrahedra) and very attractive electrochemical characteristics [51].

Rare Earth Element (REE) doped titania is recognized as an attractive goal for creation of visible light photocatalysts. Its synthesis by conventional routes is complicated by building of REE titanates as separate phases on the surface of titania grains instead of the doped material. Addition of relatively small amounts of REE(NO$_3$)$_3$·6H$_2$O (Ln = Y, Sm, Eu) to Ti(O^{i}Pr)$_4$ offered with high yields with respect to REE nitrate a heterometallic complex identified for REE = Y as YTi$_2$(NO$_3$)$_2$(O^{i}Pr)$_9$ (**4**). It is very important to note that this compound results clearly from a reaction associated with hydrolysis of titanium alkoxide, because the starting yttrium nitrate is hydrated and brings with it water for hydrolysis of Ti(O^{i}Pr)$_4$. The structure of the heterometallic complex, however, does not contain any oxo- or hydroxo-ligands, because the structures of the complexes are not bearing any "memory" of how they emerged and result simply from the most energetically stable combination of cations and ligands offered by coordination equilibrium. Again, heat-treatment of gels obtained on further hydrolytic transformation of **4** and its analogs with Eu and Sm did not lead to incorporation of REE into the anatase structure, while combustion of these precursors with an excess of Ti(O^{i}Pr)$_4$ provided doped materials that kept REE in their structure even on further annealing at 700 °C. The obtained materials showed under visible light much better photocatalytic activity compared to the P25 standard [52].

The solid-state thermal decomposition was thus even in this case a good means to avoid separation of the components at higher hydrolysis ratios.

6 Conclusions

The relative speed of hydrolysis and polycondensation can actually influence the structure and morphology of silica gels produced in organic medium with rather small amounts of catalysts. In the case of metal oxides, hydrolysis-polycondensation is a single kinetic phenomenon, leading at commonly exploited hydrolysis ratios to the nuclei of an oxide phase, possessing POM-like structure and colloid behavior—MTSALs. Oligonuclear species obtained at low hydrolysis ratios do not exhibit any pronounced stability on contact with the excess of water and are also transformed into nuclei of the corresponding oxide phases.

Application of a single-source precursor works well if its stoichiometry is maintained in the final nuclei—MTSALs and when the desired oxide phase is stable under the conditions of precursor transformation to material. The second requirement is absolute, while the first can be circumvented by solid state decomposition of the desired precursor.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

References

1. Sakka S (2022) Birth of the sol–gel method: early history. J SolGel Sci Tech 102:478–481
2. Tishchenko VE (1899) On interaction of aluminium with alcohols. J Russ Phys-Chem Soc 31:694–784

3. Smakula A (1935) Verfahren zur Erhohung der Lichtdurchlassigkeit optischer Teile durch Erniedrigung des Brechungsexponenten an den Grenzflachen dieser optischen Teile, German Pat. 685767.

4. Greenwood NN, Earnshow A (1998) The Chemistry of Elements, 2nd Ed., ISBN 0 7506 3365 4, Butterworth-Heinemann, div. of Reed Educational and Professional Publishing Ltd. Oxford, UK.

5. Essington ME (2015) Soil and Water Chemistry. An Integrative Approach, 2nd Ed., ISBN 9781032098692, CRC Press. Boca Raton.

6. Sakka S, Kozuka (2005) Handbook of Sol-Gel Science and Technology. 1 Sol-Gel Processing, 1st ed.; Kluwer Academic Publishing, Norwell, MA, USA.

7. Pope EJA, Mackenzie JD (1986) Sol-gel processing of silica: The role of the catalysts. J Non-Cryst Solids 87:185–198

8. Brinker CJ, Scherrer G (1985) Sol-gel-glass: I. Gelation and gel structure. J Non-Cryst Solids 70:301–322

9. Brinker CJ, Scherer GW (2013) Sol-Gel Science The Physics and Chemistry of Sol-Gel Processing. Academic Press, Cambridge, MA, USA

10. Hook RJ (1996) A ^{29}Si NMR study of the sol-gel polymerisation rates of substituted ethoxysilanes. J Non-Crys. Solids 195:1–15

11. Björk EM, Mäkie P, Rogström L, Atakan A, Schell N, Odén M (2018) Formation of block-copolymer-templated mesoporous silica. J Colloid Interfac Sci 521:183–189

12. Iler RK (1979) The Chemistry of Silica, 2nd Edn. John Wiley & Sons, New York, USA.

13. Polido Legaria E, Demirel Topel S, Kessler VG, Seisenbaeva GA (2015) Molecular insights into the selective action of a magnetically removable complexone-grafted adsorbent. Dalton Trans 44:1273–1282

14. Pogorilyi RP, Melnyk IV, Zub YL, Carlson S, Daniel G, Svedlindh P, Seisenbaeva GA, Kessler VG (2014) New product from old reaction: uniformmagnetite nanoparticles from iron-mediated synthesis of alkali iodides andtheir protection from leaching in acidic media. RSC Adv 4:22606–22612. https://doi.org/10.1039/C4RA02217C

15. Donhärl W, Elhofer I, Wiede P, Schubert U (1998) Elemental silicon and solid SiO give the same products as SiO_2 upon reaction with alkali-metal glycolates. J Chem Soc Dalton Trans 1998:2445–2446

16. Brook M, Brennan J, Chen J (2003) Polyol-modified silanes as precursors for silica, Patent US20040034203A1.

17. Brook MA, Chen Y, Guo K, Zhang Z, Jin W, Deisingh A, Cruz-Aguado J, Brennan J (2004) Proteins Entrapped in Silica Monoliths Prepared from Glyceroxysilanes J Sol-Gel Sci Tech 31:343–348

18. Seisenbaeva GA, Kloo L, Werndrup P, Kessler VG (2001) Electrochemical Synthesis, X-ray Single Crystal, IR Spectroscopic, and Quantum Chemical Investigation of Molybdenum and Tungsten Hexamethoxides. Inorg Chem 40:3815–3818

19. Johansson A, Roman M, Seisenbaeva GA, Kloo L, Szabo Z, Kessler VG (2000) The solution thermolysis approach to molybdenum(V) alkoxides: synthesis, solid state and solution structures of the bimetallic alkoxides of molybdenum(V) and niobium(V), tantalum(V) and tungsten(VI). J Chem Soc Dalton Trans 2000:387–394

20. Turova NY, Turevskaya EP, Yanovskay MI, Yanovsky AI, Kessler VG, Tcheboukov DE (1998) Physicochemical approach to the studies of metal alkoxides. Polyhedron 17:899–915

21. Kessler VG (2003) Molecular structure design and synthetic approaches to the heterometallic alkoxide complexes (soft chemistry approach to inorganic materials by the eyes of a crystallographer). Chem Comm 2003:1213–1222

22. Wengrovius JH, Garbauskas MF, Williams EA, Going RC, Donahue PE, Smith JF (1986) Aluminum Alkoxide Chemistry Revisited: Synthesis, Structures, and Characterization of Several Aluminum Alkoxide and Siloxide Complexes. J Amer Chem Soc 108:982–989

23. Spijksma GI, Bouwmeester HJM, Blank DHA, Fischer A, Henry M, Kessler VG (2006) Chemistry of 2,2,6,6,-Tetramethyl-3,5-heptanedione (Hthd) Modification of Zirconium and Hafnium Propoxide Precursors. Inorg Chem 13:4938–4950

24. Spijksma GI, Bouwmeester HJM, Blank DHA, Kessler VG (2004) Stabilization and destabilization of zirconium propoxide precursors by acetylacetone. Chem Comm 2004:1874–1875

25. Donat M, Seisenbaeva GA, Kessler VG (2008) Synthesis of highly sterically hindered niobium and tantalum alkoxides and their microhydrolysis in strongly basic medium. J Sol-Gel Sci Tech 48:61–65

26. Bains MS, Bradley DC (1962) Coordination complexes of metal alkoxides: part II. Metal alkoxide – ethylenediamine complexes. Can J Chem 40:2218–2228

27. Fric H, Puchberger M, Schubert U (2006) Coordination of mono- and diamines to titanium and zirconium alkoxides. J Sol-Gel Sci Tech 40:155–162

28. Sasai H, Suzuki T, Arai S, Arai T, Shibasaki M (1992) Basic character of rare earth metal alkoxides. Utilization in catalytic carbon-carbon bond-forming reactions and catalytic asymmetric nitroaldol reactions. J Amer Chem Soc 114:4418–4420

29. Mascarenhas CM, Duffey MO, Liu SY, Morken JP (1999) Simple Metal Alkoxides as Effective Catalysts for the Hetero-Aldol−Tishchenko Reaction. Org Lett 1:1427–1429

30. Baciocchi E, Illuminati G (1967) Electrophilic Aromatic Substitution and Related Reactions in Polyalkylbenzene Systems, in Progress in Physical Organic Chemistry, Streitwieser A, Taft RW Eds, John Wiley & Sons, Print ISBN:9780470833513, Online ISBN:9780470171844, https://doi.org/10.1002/9780470171844

31. Livage J, Henry M, Sanchez C (1988) Sol-gel chemistry of transition metal oxides. Progr Solid State Chem 18:259–341

32. Ribot F, Toledano P, Sanchez C (1991) Hydrolysis-condensation process of beta-diketonates-modified cerium(IV) isopropoxide. Chem Mater 3:759–764

33. Kessler VG, Spijksma GI, Seisenbaeva GA, Håkansson S, Blank DHA, Bouwmeester HJM (2006) New insight in the role of modifying ligands in the sol-gel processing of metal alkoxide precursors. A possibility to approach new classes of materials. J Sol-Gel Sci Tech 40:163–179

34. Seisenbaeva GA, Kessler VG (2014) Precursor directed synthesis – "molecular" mechanisms in the Soft Chemistry approaches and their use for template-free synthesis of metal, metal oxide and metal chalcogenide nanoparticles and nanostructures. Nanoscale 6:6229–6244

35. Cheng K, Chhor K, Brinza O, Vrel D, Kanaev A (2017) From nanoparticles to bulk crystalline solid: nucleation, growth kinetics and crystallisation of mixed oxide $Zr_xTi_{1-x}O_2$ nanoparticles. CrystEngComm 19:3955–3965

36. Cheng K, Chhor K, Kanaev A (2017) Solvent effect on nucleation-growth of titanium-oxo-alkoxy nanoparticles. Chem Phys Lett 672:119–123

37. Kessler VG, Seisenbaeva GA, Håkansson S, Unell M (2008) Chemically triggered biodelivery using metal-organic sol-gel synthesis. Angew Chem Int Ed 47:8506–8509

38. Werndrup P, Verdenelli M, Chassagneux F, Parola S, Kessler VG (2004) Powders and dense thin films of late transition metal oxide nanocomposites from structurally characterized single-source precursors. J Mater Chem 14:344–350

39. Agafonov AV, Afanasyev DA, Gerasimova TV, Krayev AS, Kashirin MA, Vinogradov VV, Vinogradov AV, Kessler VG (2016) Nanoparticle self-assembly mechanisms in the colloidal synthesis of iron titanate nanocomposite photocatalysts for environmental applications. ACS Sustain. Chem Eng 4:2814–2821

40. Seisenbaeva GA, Daniel G, Nedelec JM, Gun'ko YK, Kessler VG (2012) High surface area ordered mesoporous nano-titania by rapid surfactant-free approach. J Mater Chem 22:20374–20380

41. Seisenbaeva GA, Daniel G, Nedelec JM, Kessler VG (2013) Solution equilibrium behind room temperature synthesis of nanocrystalline titanium dioxide. Nanoscale 5:3330–3336

42. Kelp G, Tätte T, Pikker S, Mändar H, Rozhin AG, Rauwel P, Vanetsev AS, Gerst A, Merisalu M, Mäeorg U, Natali M, Persson I, Kessler VG (2016) Self-assembled SnO_2 micro- and nanosphere-based gas sensor thick films from an alkoxide-derived high purity aqueous colloid precursor. Nanoscale 8:7056–7067

43. Svensson FG, Daniel G, Tai CW, Seisenbaeva GA, Kessler VG (2020) Titanium phosphonate oxo-alkoxide "clusters": solution stability and facile hydrolytic transformation into nano titania. RSC Adv 10:6873–6883

44. Svensson F, Seisenbaeva GA, Kessler VG (2017) Mixed-Ligand Titanium "Oxo Clusters": Structural Insights into the Formation and Binding of Organic Molecules and Transformation into Oxide Nanostructures on Hydrolysis and Thermolysis. Eur J Inorg Chem 2017:4117–4122

45. Evdokimova OL, Svensson FG, Agafonov AV, Håkansson S, Seisenbaeva GA, Kessler VG (2018) Hybrid Drug Delivery Patches Based on Spherical Cellulose Nanocrystals and Colloid Titania — Synthesis and Antibacterial Properties. Nanomaterials 8:00228

46. Kessler VG (2023) Clusters or paperbags? What can we actually learn from the structure and reactivity of oligonuclear metal-oxo-alkoxide complexes? J Sol-Gel Sci Technol, https://doi.org/10.1007/s10971-023-06070-5

47. Seisenbaeva GA, Gohil S, Kessler VG (2004) Influence of heteroligands on the composition, structure and properties of homo- and heterometallic zirconium alkoxides. Decisive role of thermodynamic factors in their self-assembly. J Mater Chem 14:3177–3190

48. Westin G, Nygren M (1992) On the formation of M^{2+}-Sb^{3+}-alkoxide precursors and sol-gel processing of M-Sb oxides with M = Cr, Mn, Fe, Co, Ni, Cu and Zn. J Mater Chem 27:1617–1625

49. Vorotilov KA, Yanovskaya MI, Solovjeva LI, Valeev AS, Petrovsky VI, Vasiljev VA, Obvintzeva IE (1995) Ferroelectric capacitors for integrated circuits. Microelectronic Eng 29:41–44

50. Pazik R, Seisenbaeva GA, Wiglusz R, Kepinski L, Kessler VG (2011) Crystal structure and morphology evolution in the LaXO3, X = Al, Ga, In nano-oxide series. Consequences for the synthesis of luminescent phosphors. Inorg Chem 50:2966–2974

51. Uchiyama H, Puthusseri D, Grins J, Gribble D, Seisenbaeva GA, Pol VG, Kessler VG (2021) Single-Source Alkoxide Precursor Approach to Titanium Molybdate, $TiMoO5$, and Its Structure, Electrochemical Properties, and Potential as an Anode Material for Alkali Metal Ion Batteries. Inorg Chem 60:3593–3603

52. Svensson FG, Cojocaru B, Qiu Z, Parvulescu V, Edvinsson T, Seisenbaeva GA, Tiseanu C, Kessler VG (2021) Rare-Earth-Modified Titania Nanoparticles: Molecular Insight into Synthesis and Photochemical Properties. Inorg Chem 60:14820–14830

53. Johansson A, Kessler VG (2000) Molecular Structure Design Based on Lewis Acid-Base Interaction in the Preparation of Bimetallic Alkoxides Derived from two Electronegative Elements. The Synthesis and X-Ray Single Crystal Study of $Mo_2Ta_4O_8(OMe)_{16}$ and $Mo_4Ta_2O_8(O^iPr)_{14}$. Inorg Chem Commun 3:5–7

54. Johansson A, Kessler VG (2000) Synthesis and X-ray Single crystal Study of the Bi- and Trimetallic Alkoxides of Molybdenum(VI) and Tantalum, $Mo_2Ta_4O_8(OMe)_{16}$, $Mo_4Ta_4O_{16}(O^iPr)_{12}$ and $LiMo_4Ta_3O_{14}(O^iPr)_9(OC_2H_4OMe)_3$. Polyhedron 19:1791–1798

55. Esposito S (2019) "Traditional" Sol-Gel Chemistry as a Powerful Tool for the Preparation of Supported Metal and Metal Oxide Catalysts. Materials 12:668

56. Vrieling EG, Sun QY, Beelen TMP, Hazelaar S, Gieskes WWC, van Santen RA, Sommerdijk NAJM (2005) Controlled Silica Synthesis Inspired by Diatom Silicon Biomineralization. J Nanosci Nanotech 5:68–78