

A Brief Review on the Use of Chelation Agents in Sol-gel Synthesis with Emphasis on β -Diketones and β -Ketoesters



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Review

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Metal alkoxides are the most commonly used sol-gel process precursors. Most alkoxides show excessive reactivity towards water. That leads to rapid hydrolysis, metal hydroxide formation, and immediate precipitation. The reactivity of alkoxides can be reduced by modification with chelation agents. Chelation influences the gelation process, which is reflected in gel structure and properties of the final material. In this short review, the chelation process, the oligomerization phenomena, and the influence of the chelating agent on the gel structure are discussed. Peculiarities of the use of FTIR and NMR, as methods particularly suitable for the investigation of chelation process, are described taking ethyl acetoacetate as an example.

Keywords:

alkoxides, chelation, FTIR, NMR, sol-gel

Introduction

According to IUPAC¹, chelation is the formation of bonds between two or more separate binding sites within the same ligand and a single central atom. Thus, a chelate is a complex molecule containing a heterocyclic ring formed by chelation. The term chelate comes from the greek word $\chi\eta\lambda\acute{\alpha}$, meaning claw, such as lobster's (Fig. 1).

When two binding sites are used by the ligand for the formation of the chelate, the ligand is called bidentate, if three binding sites are used, the ligand is tridentate, etc. Monodentate ligands form a single bond to the central atom, and thus complexes with monodentate ligands are not called chelates.

Web sources most commonly associate the term chelation with a medical procedure used for the removal of heavy metals from the body, called chelation therapy². Another use for medical purposes is the preparation of contrast agents for MRI scanning³.

However, the chelation process and chelation created complexes find numerous utilizations in chemistry, chemical engineering, environmental protection, etc. Metal chelates are used in chemical vapor deposition (CVD) process, since they evaporate at relatively low temperatures (so-called metals with wings), thus enabling easy metal deposition⁴. Chelates are also used in analytical chemistry for

extraction and separation⁵, homogeneous catalysis⁶, water treatment processes⁷, and even as electroluminescent materials for displays⁸.

However, the true subject of this paper is the use of chelates and the chelation process in material science, particularly in the sol-gel process.

Sol-gel process

The sol-gel process is a synthesis procedure involving the transition of a system from a liquid "sol" into a solid "gel" phase⁹. Among other forms of ceramic materials, such as monolite ceramics, coatings, membranes, fibers, etc., the sol-gel method enables the preparation of pure and ultrafine powders at low temperatures¹⁰.

The most common precursors for the sol-gel synthesis are metallic alkoxides. The sequence of chemical reactions involved in the sol-gel process

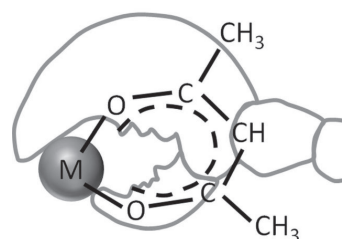


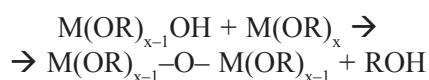
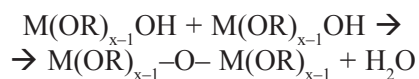
Fig. 1 – Chelation of a metal with acetilacetone. Chelate having six-membered metal acetilacetate ring is formed.

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begins with the nucleophilic substitution of the alkoxy group with hydroxyl, i.e. hydrolysis¹¹:



where M is the central metal atom, OR alkoxy group, OH hydroxyl group, while x and y are stoichiometric coefficients. What follows is water or alcohol condensation¹²:



If the coordination of metallic centers is not fully satisfied, the formation of oxygen bridges, oxolation, is competed with ololation, the formation of hydroxo bridges^{12,13}:



Finally, branched oligomers and polymers with a metal oxo (hydroxo) based skeleton, and residual reactive hydroxo and alkoxy groups are formed. When still colloidal, these structures are called sol. When they reach monolith form, entrapping the solvent and process byproducts, the formed structure is called gel.

The process is controlled through hydrolysis ratio, $h=n(H_2O)/n(M)$, temperature, catalysis, and solvents. However, when metal alkoxides highly susceptible to nucleophilic attack, such as Al, Ti or Zr alkoxides, are used as precursors, these control mechanisms are insufficient.

Two main reasons for high susceptibility to nucleophilic attack are low electronegativity and coordination unsaturation of the metal ion. Due to low electronegativity, metals show high Lewis acidity, and due to the presence of an electronegative alkoxy group, the acidity is increased¹⁴. Therefore, the metal acts as an electron pair acceptor in reaction with a Lewis base, forming a new bond. Metallic alkoxides are coordinately unsaturated since their valence does not enable the establishment of desirable coordination¹⁵, i.e., the charge of the ion does not allow the atom to be coordinated as require the relative sizes of the metal ion and surrounding ligands. Therefore, metal alkoxides show great reactivity to nucleophilic compounds such as water, which leads to rapid hydrolysis, the formation of metal hydroxide and its immediate precipitation¹⁶.

If rapid hydrolysis of one of the precursors occurs, then both homogeneity and microstructure are exacerbated. The consequence of inhomogeneity is a higher temperature and prolonged heating time requirements in the course of post-thermal treatment in order to obtain the aimed ceramic material¹⁰. Be-

sides being undesirable from the process economy and environmental protection points of view, the high thermal treatment temperatures inevitably reduce specific surface area¹⁰. Sometimes, the appearance of secondary phases due to local stoichiometry anomalies, even after prolonged thermal treatment at high temperatures, could not be avoided. On the other hand, the microstructure of the wet synthesis output affects the microstructure of the ceramic product obtained by thermal treatment¹⁰.

Chelation

In order to achieve homogeneity and microstructure of the final product, control over the sol-gel transformation is required, and that involves control over the alkoxide hydrolysis rate. In order to establish control over the hydrolysis process, alkoxides need to be modified by substituting a portion of the alkoxy groups with ligands having greater stability toward hydrolysis and enabling the expansion of the coordination sphere¹⁵, thus, occupying the sites of water attack. In such manner, complexes of type $M(OR)_{x-y}L_y$, where M is the central metal atom, OR alkoxy group, L ligand, and x and y stoichiometric coefficients, are formed. The chelation process, considering multiple substitutions of alkoxy groups with chelating ligands, can be described with the equation:



For the purpose of chelating, various molecules such as carboxylic acids¹⁷, amines¹⁸, aminopolycarboxylic acids¹⁹, diesters²⁰, β -diketones²¹, and β -ketoesters,¹⁰ etc., could be used. The latter two are particularly suitable due low price and availability²². The replacement of the alkoxy group with multi-dentate anionic ligand yields a stable bond to the metal, while the charge of the complex remains unchanged. Fig. 2 depicts the chelation process of a divalent metal ion with β -diketone.

Chelation leads to the reduced presence of hydrolysable alkoxy groups and the increase in metal coordination number, yielding steric shielding and lowering of Lewis acidity of metal center²⁰. Thus, the reactivity of the complex is reduced and the hydrolysis rate is slowed down^{23–25}.

The hydrolysis rate is also influenced by the strength of the chelate bond and the alkoxide to ligand ratio²⁶. Multiple factors contribute to the stability of the metal chelate: the number of rings that the chelating agent molecule forms with the metal ion, the size of the ring, the nature of donor atoms, resonance stabilization, and steric shielding²⁷. From the thermodynamic point of view, a significant con-

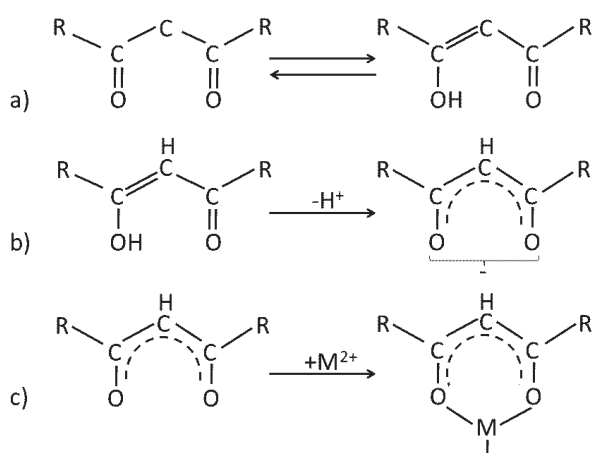


Fig. 2 – Keto-enol tautomerism of β -diketone, b) formation of diketonate anion, c) formation of the six-membered chelate ring

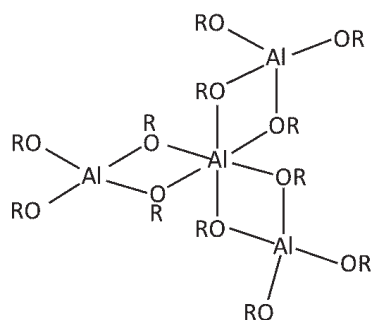


Fig. 3 – Schematic representation of aluminum alkoxide tetramer. While in monomer, aluminium is coordinated with three oxygens. In tetramer, terminal aluminium atoms are four-coordinated and central aluminium atom is six-coordinated.

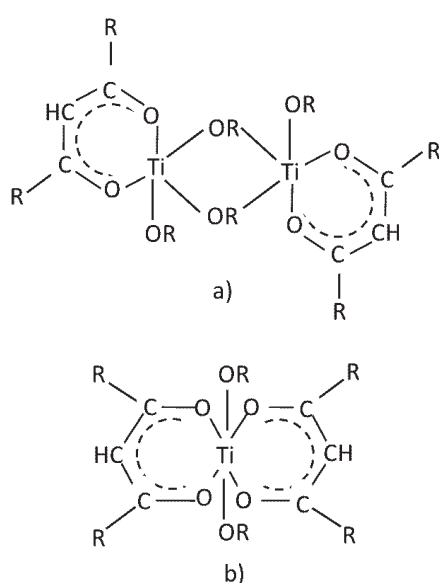


Fig. 4 – Schematic representation of a) bis-chelated dimer, and b) bis-chelated monomer of titanium alkoxide, both having six-coordinated titanium atoms

tribution to the stability of the chelate comes from the entropy increase²⁷.

Coordination of the chelating ligand also hinders condensation²⁴. The condensation process is also influenced by the reduction of reactive sites, since the degree of cross-linking drops. The chelating ligand may even impose steric limitation affecting the direction of condensation²⁶. That is reflected in the final gel structure and properties of the final material²³.

However, it should be mentioned that there are opinions that hydrolysis and subsequent condensation do not decrease, but rather increase with the introduction of chelating ligands²⁸. The same authors claim that the gelation process has no direct relation with the hydrolysis and condensation processes²⁹, and see the role of chelating ligands as surfactants stabilizing oxide nanoparticles generated by hydrolysis and condensation³⁰. Such opinions have been disproved by numerous papers, some of them by this autor, e.g.³¹

When factors influencing the gel structure are considered, alkoxide oligomerization should also be mentioned. Namely, beside susceptibility to nucleophilic attack, another consequence of disagreement between coordination and valence is oligomerization. Since metal alkoxides have unsaturated coordination, they tend to expand their coordination via formation of alkoxo (OR) bridges, thus forming oligomeric molecular structure (Fig. 3). Therefore, many alkoxides exist as dimers, trimers or tetramers^{32,33}. The degree of oligomerization is proportional to the size of the metal atom, and inversely proportional to the oxidation state and steric demand of the alkoxy group³⁴. The degree of oligomerization influences alkoxide reactivity, since the increased degree of oligomerization lowers the capability to coordinate donor molecules³⁴. Coordination expansion could also be realized through solvate formation¹¹, e.g., $Zr(Oi-Pr)_4(i-PrOH)_2$ is formed when zirconium *iso*-propoxide is dissolved in isopropanol.

Metal alkoxides tendency toward oligomerization is retained after chelation³⁵. However, besides reducing the metal ion accessibility to water, the chelation affects the degree of oligomerization, and thus influences the structure of the obtained chelate³⁵. At lower chelation agent to alkoxide ratio, the degree of oligomerization remains unchanged as far as the chelation agent is able to provide the increase in metal atoms coordination saturation (Fig. 4a). At increased chelation agent to alkoxide ratio, metal atom saturation could be achieved with the chelation alone, thus leading to the reduction of oligomerization degree (Fig. 4b), which is the reason for the prevalence of monomeric chelate molecules at high chelation agent to alkoxide ratio.

Influence of the chelation agent on the structure and microstructure of the final product

The amount of chelating agent suitable for addition to the alkoxide depends on the ratio of the chelating agent and alkoxide at which the coordination saturation of alkoxide molecule is achieved. However, while partial replacement of alkoxy groups with chelating agent in the presence of a moderate amount of water will lead to slow condensation²⁵, if alkoxy groups are completely replaced with chelating agents, hydrolysis and thus condensation could be completely prevented³⁷.

But even if particular chelate stoichiometry is aimed through the chelation process, different oligomers, having various oligomerization degrees and various chelation agent to alkoxide ratios, as well as various isomers of those chelates, could be present in the solution³⁸. Their quantitative relationships, besides alkoxide and chelating agent, stoichiometry and oligomerization, depend on temperature and solvent^{35,39}, and even on the kinetics of the chelation process since the process of attaining equilibria could be slow. The sol-gel synthesis process conditions are usually such that no crystallization of chelates occurs. However, chelates could form crystal structures³⁸.

In the presence of a moderate amount of water, the hydrolysis of complexes with ligands forming stable chelates affects almost exclusively alkoxy groups²⁵. Therefore, since the presence of the chelating agent changes the functionality of the alkoxide, it affects the hydrolysis and condensation process, and thus the gel network formed later through hydrolysis and condensation⁴⁰. Another way of affecting the gel morphology through the influence on the polycondensation process is the limitation of polymer chain development in directions in space shielded by the chelation agent²⁵. Finally, ligands can bear groups with additional functionality, i.e., polymerizable groups such as metacrylates⁴¹, which can also affect the gel structure. Namely, when ligands with unsaturated bonds are used, gel network may be modified in a sense that inorganic segments of the gel network with $-M-O-M-$ bridges are linked through polymerized ligands⁴². Also, a higher chelation agent to alkoxide ratio and a moderate amount of water enable the obtaining of small colloidal particles, while a decrease in the chelation agent to alkoxide ratio and an increase in water amount will yield larger sol particles¹¹. Besides particle size, it was established that the chelating agents affect the shape of the final nanopowder⁴³. It has also been noted that chelating agents influence agglomeration and precipitation of particles in the course of hydrolysis, as the ratio of chelating agent to alkoxide increased, the agglomeration decreased²⁴.

Therefore, variations in chelate structures affect the processes of hydrolysis and condensation, and, in turn, the structure and microstructure of the obtained gel, the crystallization process, the phases formed, and the final properties of the material³⁸. Thus, chelation enabled the obtaining of, e.g., organized porous alumina with a denser and isotropic structure⁴⁴, alumina aerogels⁴⁵, hierarchically porous TiO_2 monoliths⁴⁶, and compact and smooth yttria thin films⁴⁷. Of course, thermal treatment also has great influence on the properties of the obtained material. Namely, in the course of thermal treatment, the organic phase is removed. The intensity of this process is controlled by thermal treatment regime and could greatly affect texture, microstructure, and structure of the final material.

Methods suitable for the investigation of the chelation process

In the course of chelate formation, the chelating agent molecule can lose a hydrogen atom, electron delocalization occurs, and a ring is formed. Such changes enable the monitoring of chelation, as well as subsequent hydrolysis. Some of the best methods for this task are nuclear magnetic resonance (NMR) and Fourier transformed infrared spectroscopy (FTIR)^{23,36,38}. A good example of utilizing FTIR and NMR for the investigation of the chelation process is the preparation of chelates with β -diketones or β -ketoesters. Those molecules undergo keto-enol tautomerism, i.e., equilibrium between two tautomers, keto and enol exists. The process is typical for aldehydes and ketones when the carbon adjacent to the carbonyl group ($C=O$), α -carbon, possesses a hydrogen (α -hydrogen). The transformation process involves the movement of α -hydrogen to carbonyl oxygen, which thus becomes a hydroxyl group, and the formation of carbon-carbon double bond (Fig. 5)²³.

As in most ketones and ketoesters, the keto form predominates in ethyl acetoacetate⁴⁰. However, in the course of keto-enol interconversion, the deprotonated intermediate, enolate anion, appears. Being a strong nucleophile, in the presence of alkoxide, monocharged enolate substitutes its alkoxy groups, thus forming a chelate (Fig. 5). The chelation process influences the keto-enol equilibrium, shifting it strongly towards the enolic form²³ since it is removed from the process by formation of chelate.

The described processes, keto-enol equilibria, chelation, as well as hydrolysis, could be investigated using infra-red spectroscopy. The most characteristic absorption bands of keto tautomer of ethyl acetoacetate are at $\sim 1,750$ – $1,720$ cm^{-1} due to the

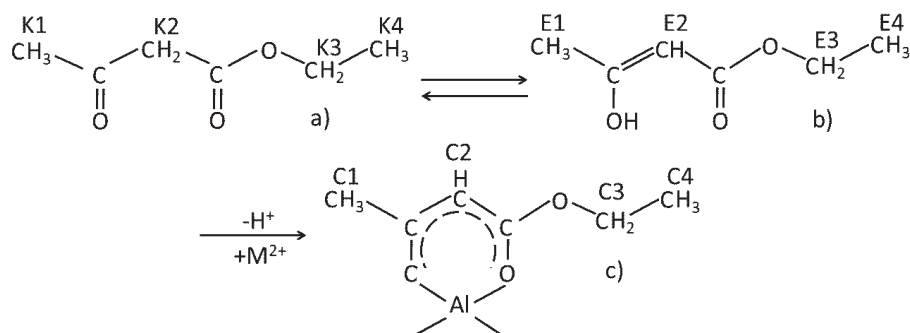


Fig. 5 – Keto-enol tautomerism of ethyl acetoacetate and formation of a chelate between metal alkoxide and ethyl acetoacetate a) keto tautomer; b) enol tautomer; c) chelate. Labels are introduced for ^1H NMR peaks description.

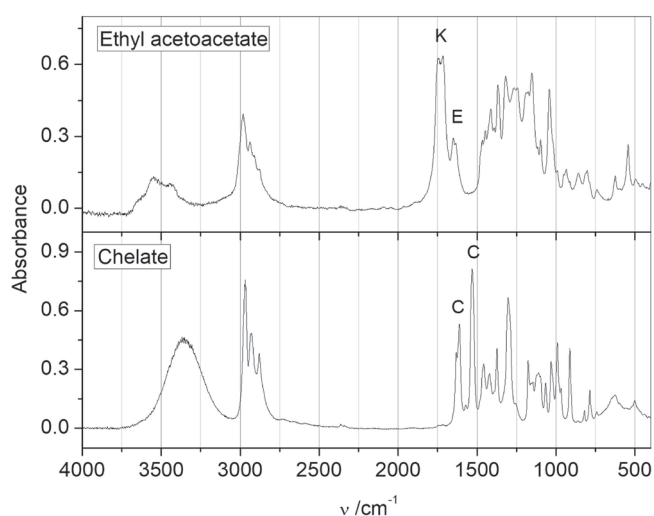


Fig. 6 – FTIR spectra of ethyl acetoacetate and aluminium chelate. K – typical keto tautomer bands, E – typical enol tautomer bands, C – typical chelate bands.

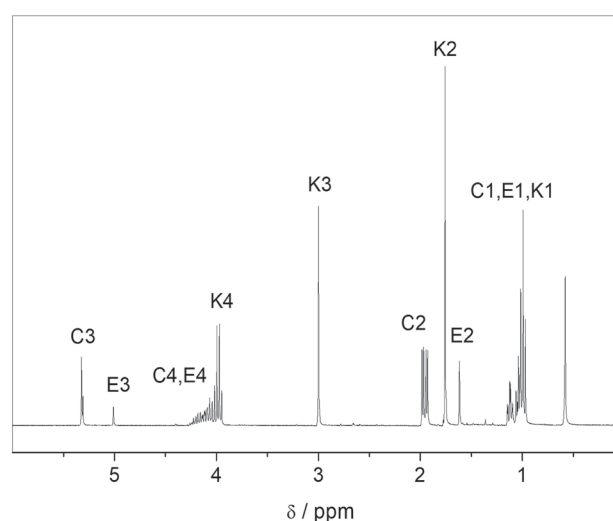


Fig. 7 – ^1H NMR spectra of sample containing keto and enol tautomer of ethyl acetoacetate and aluminium chelate. Peaks are labeled according to Fig. 5.

C=O stretching vibration of two carbonyl groups. The most characteristic band of enol tautomer is at $\sim 1,650\text{ cm}^{-1}$ due to hydrogen bonding between the C=O and hydroxyl group, as well as at $\sim 1,630\text{ cm}^{-1}$ due to alkene bond in conjugation with a carbonyl group (Fig. 6). Forming a chelate with, e.g., Al Eaa, shows characteristic bands at $\sim 1,610\text{ cm}^{-1}$ due to C–O vibration in enolate bonded to Al, as well as a band at $\sim 1,525\text{ cm}^{-1}$ due to C–C vibration of six membered ring of the complex (Fig. 6)^{23,47}. The same bands appear at similar wavenumbers for Ti chelated with ethyl acetoacetate^{22,36}.

However, beside qualitative, ^1H NMR method enables even quantitative interpretation of the keto – enol–bonded enolate relationships. In the course of ethyl acetoacetate keto to enol transformation, one hydrogen atom attached to α -carbon between two carbonyl groups moves to carbonyl oxygen. That causes the disappearance of methylene ($-\text{CH}_2-$) protons signal at 3 ppm (Fig. 7, K3) and the appearance of methyne proton signal at 5 ppm (Fig. 7,

E3). When bonded in Al chelate, enolate methyne proton signal shifts to 5.22 ppm (Fig. 7, C3). All other resonances also experience shifts when one tautomer transforms to another or when enolate bonds with metal forming chelate²³. Again, similar spectral changes occur when Ti chelate with ethyl acetoacetate is formed³⁶.

Additionally, if ^1H NMR resonance signals that should otherwise be singlets, such as methyne proton between two carbonyl groups (Fig. 7, K1, E1), exhibit multiplets (Fig. 7, C2), that is an indication of the presence of either inequivalent chelating sites or of various chelate molecules³⁶. The variations in the intensity of these signals with the chelation agent to metal alkoxide ratio could enable the deduction of the compounds (various oligomers and isomers) present, as well as their quantitative relationships³⁶. In order to do so, the deconvolution of spectral segments with characteristic signals and mass balance procedure should be performed³⁶.

^{13}C NMR, ^{27}Al NMR, as well as 2D NMR methods also proved as very useful methods in the investigation of the chelation process, as well as further hydrolysis and condensation processes^{36,47}.

Conclusion

In this review, sol-gel synthesis control using the chelation process is described. It is shown how chelation affects the rate of hydrolysis, the degree of oligomerization, the hydrolysis products, and the gel structure. The methods providing insight into the structure of the complexes formed are addressed. The importance of chelate processes investigations for the control of the sol-gel synthesis outcome is emphasized.

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References

- McNaught, A. D., Wilkinson, A., IUPAC compendium of chemical terminology, 2nd ed. (the „Gold Book“), Blackwell Scientific Publications, Oxford, 1997. doi: <http://goldbook.iupac.org/html/C/C01012.html> (15. 10. 2018.)
- Swaran, J. S. F., Pachauri, V., Chelation in metal intoxication, *Int. J. Environ. Res. Public. Health* **7** (2010) 2745. doi: <https://doi.org/10.3390/ijerph7072745>
- Wiener, E., Brechbiel, M. W., Brothers H., Magin, R. L., Gansow, O. A., Tomalia, D. A., Leuterbur, P. C., Dendrimer-based metal chelates: A new class of magnetic resonance imaging contrast agents, *Magn. Reson. Med.* **31** (1994) 1. doi: <https://doi.org/10.1002/mrm.1910310102>
- Hampden-Smith, M. J., Kodas, T. T., Chemical vapor deposition of metals: Part 1. An overview of CVD processes, *Chem. Vap. Deposition* **1** (1995) 8. doi: <https://doi.org/10.1002/cvde.19950010103>
- Ding, X., Liu, Q., Hou, X., Fang, T., Supercritical fluid extraction of metal chelate: A review, *Rev. Anal. Chem.* **47** (2017) 99. doi: <https://doi.org/10.1080/10408347.2016.1225254>
- Breit, B., Chelating bidentate ligands for homogeneous catalysis, *Angew. Chem. Int. Ed.* **44** (2005) 6816. doi: <https://doi.org/10.1002/anie.200501798>
- Kryvoruchko, A., Kornilovich, B., Yurlova, L., Purification of water containing heavy metals by chelating-enhanced ultrafiltration, *Desalination* **144** (2002) 243. doi: [https://doi.org/10.1016/S0011-9164\(02\)00319-3](https://doi.org/10.1016/S0011-9164(02)00319-3)
- Chen, C. H., Shi, J., Metal chelates as emitting materials for organic electroluminescence, *Coord. Chem. Rev.* **171** (1998) 161. doi: [https://doi.org/10.1016/S0010-8545\(98\)90027-3](https://doi.org/10.1016/S0010-8545(98)90027-3)
- Sajjadi, S. P., Sol-gel process and its application in nanotechnology, *J. of Polym. Eng. Tech.* **13** (2005) 38.
- Kurajica, S., Tkalčec, E., Šipušić, J., Matijašić, G., Brnardić, I., Simčić, I., Synthesis and characterization of nanocrystalline zinc aluminate spinel by sol-gel technique using modified alkoxide precursor, *J. Sol-Gel Sci. Technol.* **46** (2008) 152. doi: <https://doi.org/10.1007/s10971-008-1707-2>
- Livage, J., Basic principles of sol-gel chemistry, In: Aegerter, M. A., Menning, M. (Eds.), *Sol-gel technologies for glass producers and users*, Springer, New York, 2004, pp 3-14.
- Brinker, C. J., Scherrer, G. W., *Sol-gel science. The physics and chemistry of sol-gel processing*, Academic press, Boston, 1990, pp 108.
- Owens, G. J., Singh, R. K., Foroutan, F., Alqaysi, M., Han, C.-M., Mahapatra, C., Kim, H.-W., Knowles, J. C., Sol-gel based materials for biomedical applications, *Prog. Mater. Sci.* **77** (2016) 1. doi: <https://doi.org/10.1016/j.pmatsci.2015.12.001>
- Haridas, M. M., Bellare, J. R., Gellability zone for aluminium alkoxides, *Ceram. Int.* **25** (1999) 613. doi: [https://doi.org/10.1016/S0272-8842\(98\)00074-1](https://doi.org/10.1016/S0272-8842(98)00074-1)
- Velez, K., Quinson, J. F., Fenet, B., Modification study of aluminum sec-butoxide by acrylic acid, *J. Sol-Gel Sci. Tech.* **16** (1999) 201. doi: <https://doi.org/10.1023/A:1008767218134>
- Rodriguez, J. A., Fernandez-Garcia, M. (eds.), *Synthesis, properties, and applications of oxide nanomaterials*, J. Wiley & Sons, Hoboken, 2007, pp 95.
- Predoana, L., Jitianu, A., Malic, B., Zaharescu, M., Study of the gelling process in the La-Co-citric acid system, *J. Am. Ceram. Soc.* **95** (2012) 1068. doi: <https://doi.org/10.1111/j.1551-2916.2011.04965.x>
- Bockmeyer, M., Löbmann, P., Formation, densification and properties of sol-gel TiO₂ films prepared from triethanolamine-chelated soluble precursor powders, *J. Sol-Gel Sci. Tech.* **45** (2008) 251. doi: <https://doi.org/10.1007/s10971-007-1642-7>
- Hashem, A. M., Abdel-Ghany, A. E., Abuzeid, H. M., El-Tawil, R. S., Indris, S., Ehrenberg, H., Mauger, A., Julien, C. M., EDTA as chelating agent for sol-gel synthesis of spinel LiMn₂O₄ cathode material for lithium batteries, *J. Alloys Compd.* **737** (2018) 758. doi: <https://doi.org/https://doi.org/10.1016/j.jallcom.2017.12.153>
- Lichtenberger, R., Baumann, S. O., Bendova, M., Puchberger, M., Schubert, U., Modification of aluminium alkoxides with dialkylmalonates, *Monatsh. Chem.* **141** (2010) 717. doi: <https://doi.org/10.1007/s00706-010-0317-1>
- Kurajica, S., Lozić, I., Pantaler, M., Thermal decomposition of calcium (II) bis(acetylacetonate) n-hydrate, *Polimeri* **35** (20014) 4.
- Kurajica, S., Minga, I., Mandić, V., Matijašić, G., Nanocrystalline anatase derived from modified alkoxide meso-structured gel, *J. Therm. Anal. Calorim.* **124** (2016) 645. doi: <https://doi.org/10.1007/s10973-015-5188-6>
- Kurajica, S., Mali, G., Gazivoda, T., Šipušić, J., Mandić, V., A spectroscopic study of calcium aluminate gels obtained from aluminium sec-butoxide chelated with ethyl acetoacetate in various ratios, *J. Sol-Gel Sci. Technol.* **50** (2009) 58. doi: <https://doi.org/10.1007/s10971-009-1905-6>

24. Maeng, W. Y., Yoo, M., Effect of chelating agents on the stability of nano-TiO₂ sol particles for sol-gel coating, *J. Nanosci. Nanotechnol.* **15** (2015) 8429. doi: <https://doi.org/10.1166/jnn.2015.11462>
25. Turova, N. Y., Turovskaya, E. P., Kessler, V. G., Yanovskaya, M. I., The chemistry of metal alkoxides, Kluwer Academic Publishers, New York, 2002, pp 87–96.
26. Danks, A., Hall, S. R., Schnepf, Z., The evolution of sol-gel chemistry as a technique for material synthesis, *Mater. Horiz.* **3** (2016) 91. doi: <https://doi.org/10.1039/C5MH00260E>
27. Lehman, D. S., Some principles of chelation chemistry, *Soil Science Society of America Proceedings* **27** (1963) 167.
28. Kessler, V. G., Spijksma, G. I., Seisenbaeva, G. A., Hakanson, S., Blank, D. H. A., Bouweester, H. J. M., New insights 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** (2006) 163. doi: <https://doi.org/10.1007/s10971-006-9209-6>
29. Kessler, V. G., Sol-gel precursors, In: Levy, D., Zayat, M. (Eds), *Sol-Gel Handbook, Vol. 1 Synthesis and Processing*, Wiley-VCH, Weinheim, 2015, pp 195–216.
30. Seisenbaeva, G. A., Kessler, V. G., Precursor directed synthesis: “Molecular” mechanisms in the soft chemistry approaches and their use for the template-free synthesis of metal, metal oxide and metal chalcogenide nanoparticles and nanostructures, *Nanoscale* **6** (2014) 6229. doi: <https://doi.org/10.1039/C3NR06336D>
31. Kurajica, S., Gazivoda Kraljević, T., Mali, G., Simčić, I., Mandić, V., Minga, I., Multinuclear magnetic resonance study on aluminium *sec*-butoxide chelated with ethyl acetoacetate in various amounts, *Croat. Chem. Acta* **92** (2019) 17. doi: <https://doi.org/10.5562/cca3426>
32. Kriz, O., Casensky, B., Lycka, A., Fusek, J., Hermanek, S., ²⁷Al NMR behavior of aluminium alkoxides, *J. Mag. Res.* **60** (1984) 375. doi: [https://doi.org/10.1016/0022-2364\(84\)90048-9](https://doi.org/10.1016/0022-2364(84)90048-9)
33. Wengrovius, J. H., Garbaskas, M. F., Williams, E. A., Going, R. C., Donahue, P. E., Smith, J. F., Aluminium alkoxide chemistry revisited: Synthesis, structures, and characterization of several aluminium alkoxide and siloxide complexes, *J. Am. Chem. Soc.* **108** (1986) 982. doi: <https://doi.org/10.1021/ja00265a024>
34. Lichtenberger, R., Schubert, U., Chemical modification of aluminium alkoxides for sol-gel processing, *J. Mater. Chem.* **20** (2010) 9287. doi: <https://doi.org/10.1039/C0JM00993H>
35. Lichtenberger, R., Puchberger, M., Baumann, S. O., Schubert, U., Modification of aluminium alkoxides with β -ketoesters: New insights into formation, structure and stability, *J. Sol-Gel Sci. Technol.* **50** (2009) 130. doi: <https://doi.org/10.1007/s10971-008-1890-1>
36. Kurajica, S., Škorić, I., Lozić, I., Mandić, V., Ethyl acetoacetate ligand distribution in the course of titanium n-butoxide chelation, *Mat. Chem. Phys.* **147** (2014) 1058. doi: <https://doi.org/10.1016/j.matchemphys.2014.06.059>
37. Kurajica, S., Minga, I., Mandić, V., Mužina, K., Sol-gel preparation of nanocrystalline titania photocatalyst using ethyl acetoacetate modified Ti(n-BuO)₄ precursor, *Eur. Chem. Bull.* **6** (2017) 155. doi: <https://doi.org/10.17628/ecb.2017.6.155-162>
38. Kurajica, S., Popović, J., Gazivoda Kraljević, T., Tkalčec, E., Simčić, I., Mandić, V., Altomare, A., Moliterni, A., Rocquefelte, X., A structural investigation of tris(ethyl acetoacetate)aluminium (III), *J. Sol-Gel Sci. Technol.* **71** (2014) 217. doi: <https://doi.org/10.1007/s10971-014-3345-1>
39. Mandić, V., Kurajica, S., The influence of solvents on sol-gel derived calcium aluminate, *Mater. Sci. Semicond. Process.* **38** (2015) 306. doi: <https://doi.org/10.1016/j.mssp.2015.01.004>
40. Nass, R., Schmidt, H., Synthesis of an alumina coating from chelated aluminium alkoxides, *J. Non-Cryst. Solids* **121** (1990) 329. doi: [https://doi.org/10.1016/0022-3093\(90\)90153-D](https://doi.org/10.1016/0022-3093(90)90153-D)
41. Ivanovici, S., Puchberger, M., Fric, H., Kickelbick, G., Coordination behavior of acetoacetate ligands with attached methacrylate groups containing alkyl-spacers of different length to titanium and zirconium alkoxides, *Monatsh. Chem.* **138** (2007) 529. doi: <https://doi.org/10.1007/s00706-007-0632-3>
42. Hoebbel, D., Reinert, T., Schmidt, H., Arpac, E., On the hydrolytic stability of organic ligands in Al-, Ti- and Zr-alkoxide complexes, *J. Sol-Gel Sci. Technol.* **10** (1997) 115. doi: <https://doi.org/10.1023/A:1018305811088>
43. Balandeh, M., Asgari, S., Synthesis and characterization of LiNiO₂ nanopowder with various chelating agents, *J. Nanomater.* Volume 2010, Article ID 695083. doi: <https://doi.org/10.1155/2010/695083>
44. Diaz, I., Gonzales-Pena, V., Marquez-Alvarez, C., Perez-Pariante, J., Kikkides, E. S., Investigation of organized porous alumina by transmission electron spectroscopy, *Stud. Surf. Sci. Catal.* **158** (2005) 541. doi: [https://doi.org/10.1016/S0167-2991\(05\)80383-0](https://doi.org/10.1016/S0167-2991(05)80383-0)
45. Pierre, A., Begag, R., Pajonk, G., Structure and texture of alumina aerogel monoliths made by complexation with ethyl acetoacetate, *J. Mat. Sci.* **34** (1999) 4937. doi: <https://doi.org/10.1023/A:1004703504103>
46. Hasegawa, G., Studies on porous monolithic materials prepared via sol-gel processes, Springer, Tokio, 2013, pp 107–119.
47. Tadanaga, K., Iwami, T., Tohge, N., Minami, T., Precursor structure and hydrolysis-gelation process of Al(O-*sec*-Bu)₃ modified with ethylacetoacetate, *J. Sol-Gel Sci. Technol.* **3** (1994) 5. doi: <https://doi.org/10.1007/BF00490143>