“Traditional” Sol–Gel: The Chemistry of Alkoxides

Original
“Traditional” Sol–Gel: The Chemistry of Alkoxides / Esposito, S. - In: Sol–Gel Synthesis Strategies for Tailored Catalytic Materials[s.l] : Springer, 2023. - ISBN 978-3-031-20722-8. - pp. 13-20 [10.1007/978-3-031-20723-5_2]

Publisher:
Springer

Published
DOI:10.1007/978-3-031-20723-5_2

Chapter 2

Traditional sol-gel: the chemistry of alkoxides

Abstract

Nowadays, sol-gel chemistry collects plenty of fascinating strategies to prepare materials from solution state precursors, however it originated with the hydrolysis and condensation of metal alkoxides. The first metal alkoxide was prepared from silicon tetrachloride ($SiCl_4$) and alcohol by Ebelman [1] opening a new frontier for the inorganic chemistry. Surprisingly, the term sol-gel first appeared almost 100 years later, around 1930, by the studies of Graham and Hurd [2,3]. They proved that water in silica gel can be exchanged with organic solvent confirming the theory that a gel can be depicted as a solid network with continuous porosity.
Starting from this knowledge, highly porous silica, lightweight but mechanically rigid, was prepared by supercritical drying process, suppressing shrinkage otherwise possible with solvent evaporation [4].
Although in the 1930s Geffken brought the sol-gel processing to an industrial scale through the preparation of oxide layers by dip coating, it was not until the 1970s that significant efforts were made to synthesise materials using the sol-gel approach [5]. Since the plentiful of synthesized and commercially available silicon alkoxides, the silica-based materials are still representative of the sol-gel synthesis. The transition metal oxide can also be prepared by sol–gel processing, but the different chemical reactivity of transition metal alkoxides has strong structural consequences. This chapter will recall the fundamental rules of hydrolysis and condensation reaction, the description of mechanism of the substitution reactions will be a guideline to the understand the greater reactivity in the polymerization reaction in the case where M is a transition metal with respect to the case in which M = Si.

Keywords: silicon alkoxides, transition metal alkoxides, hydrolysis and condensation reactions

2.1 Hydrolysis and condensation reactions: an overview

In most traditional aqueous sol-gel approach, metal alkoxides, M(OR)n, are considered the optimal precursors. Indeed, in the presence of water, they are readily converted into the corresponding oxides through the hydrolysis and condensation reactions that, in a way, take us back to the polymerisation reactions of organic compounds. In details, three reactions are representative of the sol-gel chemistry. The reaction that forms the starting point of the process is the hydrolysis reaction (Scheme 2.1, reaction 1) where an alkoxide group (OR) is substituted with a hydroxyl group (OH). The condensation reaction, which leads to the formation of M-O-M bonds, can proceeds with the elimination of water (Scheme 2.1, reaction 2) when two hydroxyl groups are involved, or with the elimination of alcohol (Scheme 2.1, reaction 3) if a hydroxyl group reacts with an alkoxy group. Reverse reactions, esterification and alcoholic or hydrolytic depolymerisation contribute, to a greater or lesser extent depending on the reaction conditions, to determining the final gel structure.
Being water and alkoxide immiscible in all proportions, the reactions just mentioned take place in alcoholic solutions, usually the parent alcohol is used.

$$\equiv M-OR+HOH \rightleftharpoons \equiv M-OH+ROH \qquad (1)$$

$$\equiv M-OH+\equiv M-OH \rightleftharpoons \equiv M-O-M\equiv +HOH \qquad (2)$$

$$\equiv M-OH+\equiv M-OR \rightleftharpoons \equiv M-O-M\equiv +ROH \qquad (3)$$

Scheme 2.1 Representative reactions of the sol-gel process; (1) hydrolysis of an alkoxy group, (2) water producing condensation and (3) alcohol producing condensation

The rational design of a catalyst, like any other material prepared by the sol-gel method, should always start from a knowledge of the mechanisms and kinetics of these reactions. Moreover, the choice of chemical strategy must be directed toward easily handled, available and low-cost precursors. Before proceeding into a more detailed description of hydrolysis and condensation reactions, we must necessarily make a distinction between silicon alkoxides and transition metal alkoxides since their chemistry is different.

2.2 Silicon alkoxides

As mentioned in the previous chapter, Mx(OR)y are the most commonly used precursors in the sol-gel synthesis of oxide based system. The physicochemical properties and reactivity of Mx(OR)y compounds are determined by the nature and size of the alkyl groups, which gives even greater versatility to the sol-gel method. This is especially true in the case of silicon for which a vast number of precursors can be chosen [6,7]. Moreover, in the preparation of a multicomponent system, mixed alkoxide can be advantageous to avoid homo-condensation phenomena.

Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) are the most widely used starting precursors for the preparation of silica-based materials by sol-gels. We can, therefore, consider TEOS to look deeper into the mechanisms of the reactions mentioned above (Scheme 2.1, reactions 1-3).

As showed in Fig. 2.1, the hydrolysis proceeds via a typical SN2 reaction mechanism: first the silicon atom bearing a partial positive charge is attached by the oxygen of a water molecule, resulting in a hypervalent state [8]. In the next step, a proton from H_2O is transferred to the ester bond of an opposite alkoxyl group, generating a better leaving group. The net result is a partially hydrolysed tetraethoxysilane and the release of an alcohol molecule. Oligomeric species (monomer, dimer, linear trimer, cyclic trimer, cyclic tetramer and higher order rings) characterized by siloxane bonds are formed by either an alcohol producing condensation reaction, Fig. 2.2, or a water producing condensation reaction by a SN2 reaction mechanism.

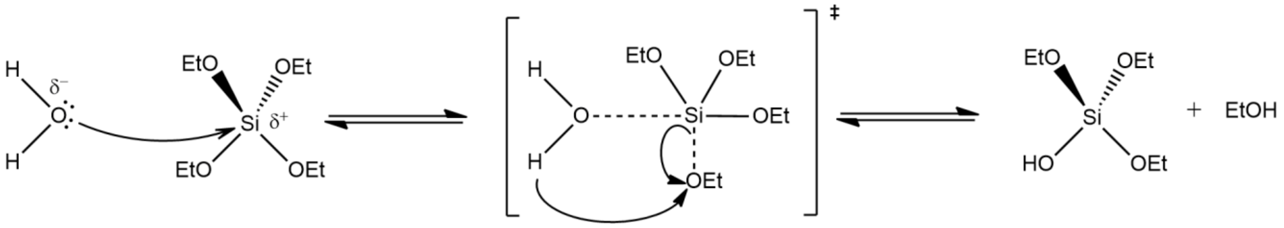

Figure 2.1 Mechanism of hydrolysis of tetraethoxysilane, Si(OEt)4

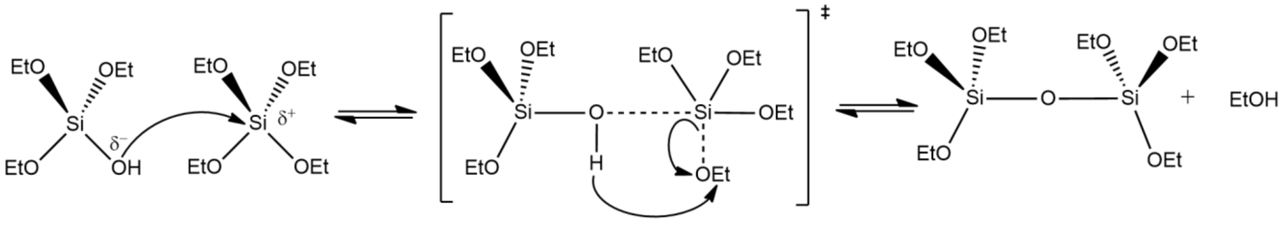

Figure 2.2 Mechanism of alcohol producing condensation of tetraethoxysilane, $Si(OEt)_4$

As general rule, the extent of nucleophilic reactions is governed by the electronegativity of the metal atom, its coordination number and the steric hindrance of alkoxide groups [8]. The reaction rate, on the other hand, increases if the coordination number of the central atom exceeds its valence number [9]. The difference N - Z, where N and z indicate the coordination number and the charge of the element M, respectively, accounts for the degree of unsaturation of the metal coordination. Compared to transition metals, silicon is less electropositive and the resulting reduced partial charge makes silicon less susceptible to nucleophilic attack [10]. Moreover, N - Z is equal to zero since the coordination number coincides with its valence (+IV). The addition of an acid or basic catalyst is, therefore, required to speed up the kinetics of the hydrolysis and condensation reactions.

The role of the catalyst was studied by E.J.A. Pope and J.D. Mackenzie [11], highlighting not only the effects of the hydronium ion and hydroxyl ion on gel times, but also the effects of the conjugated base, particularly the fluoride F^-. The significant decrease in gelation time observed with hydrofluoric acid was attributed to the ability of the fluorine anion to modify silicon alkoxide to form a partially fluorinated silicon alkoxide more prone to nucleophilic attack. This study provided a major breakthrough in understanding the reaction mechanisms and the factors that may contribute to the final gel structure.

2.2.1 Acid and base catalysis

Because hydrolysis and condensation reactions are very slow at neutral pH, the sol-gel process involving silica precursors generally employs acid or basic catalysts [12].

As in classical acid catalysis, the first step is the protonation of an oxygen atom of the Si-OR group (Figure 2.3a), which makes the central silicon atom more susceptible to water attack (in hydrolysis reactions) [13]. From the pentacoordinate transition state, a partially hydrolysed alkoxide is obtained (with inversion of the silicon tetrahedron) through the breaking of a Si-O bond, release of an alcohol molecule and regeneration of the catalyst, Figure 2.3a

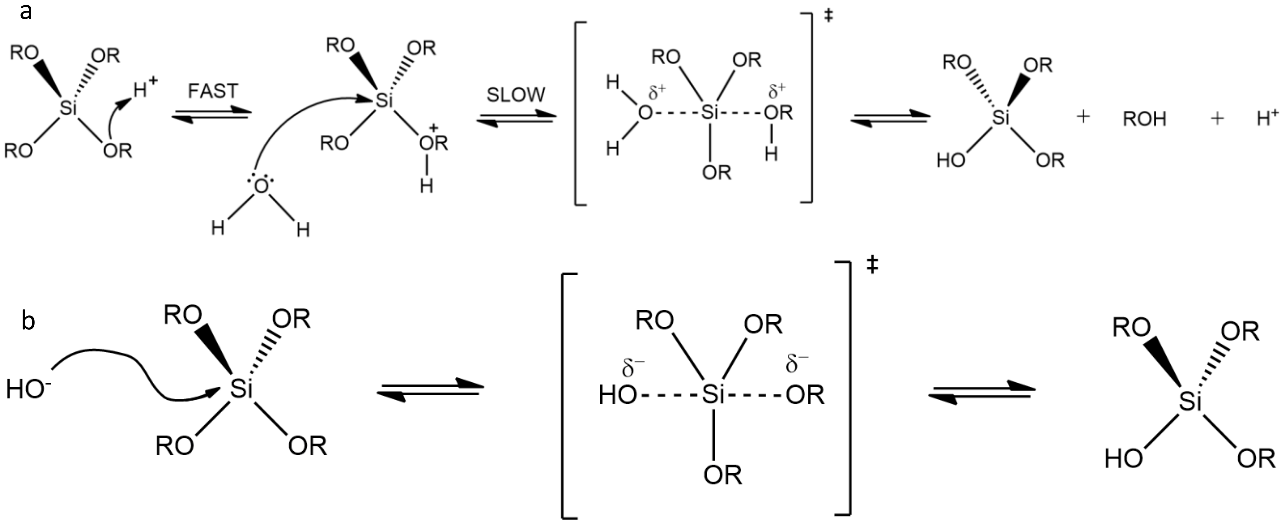

Figure 2.3 Mechanism of (a) acid catalysed hydrolysis of silicon alkoxides and (b) base catalysed hydrolysis of silicon alkoxides

Following the above path, we should expect the rate of hydrolysis to increase with substituents that decrease the steric hindrance around silicon and promote electron donation toward silicon

In basic conditions, a pentacoordinate transition state is obtained, Figure 2.3b which, unlike acid catalysis, is characterized by a negative charge. For this reason, hydrolysis is favoured by electron withdrawing substituents. The hydrolysis rate may increase with the extent of both hydrolysis and condensation because inversion of configuration is not required.

The higher reactivity of TMOS compared with TEOS is explained by the smaller size of the ethoxy group compared with the methoxy group. Reactivity decreases as the size of the OR group increases following the order $Si(OMe)_4 > Si(OEt)_4 > Si(OnPr)_4 > Si(OiPr)_4 > Si(OnBu)_4$. The possible substitution of -OR groups for -R' groups ($R'_xSi(OR)_{4-x}$) changes the electronic density around the silicon and brings us back to consider the impact of inductive effects on precursor reactivity. Effects that, as previously discussed, proceed in opposite directions for acidic and basic catalysis. The seemingly simple fact of being able to replace OR groups with nonhydrolyzable groups has several far-reaching chemical consequences in terms of catalyst engineering. In principle, it is possible to govern the textural properties and introduce specific functionalities on the surface [14, 15]. The electron density at the silicon atom decreases in the following order: alkyl group, alkoxy group, hydroxyl group and Si-O-Si group.

Similar consideration can be done for the condensation reactions whose extent depend on the hydrolysis degree, Fig 2.4. Unlike hydrolysis, where both steric and inductive factors are relevant, the condensation reaction is mainly influenced by steric effects.

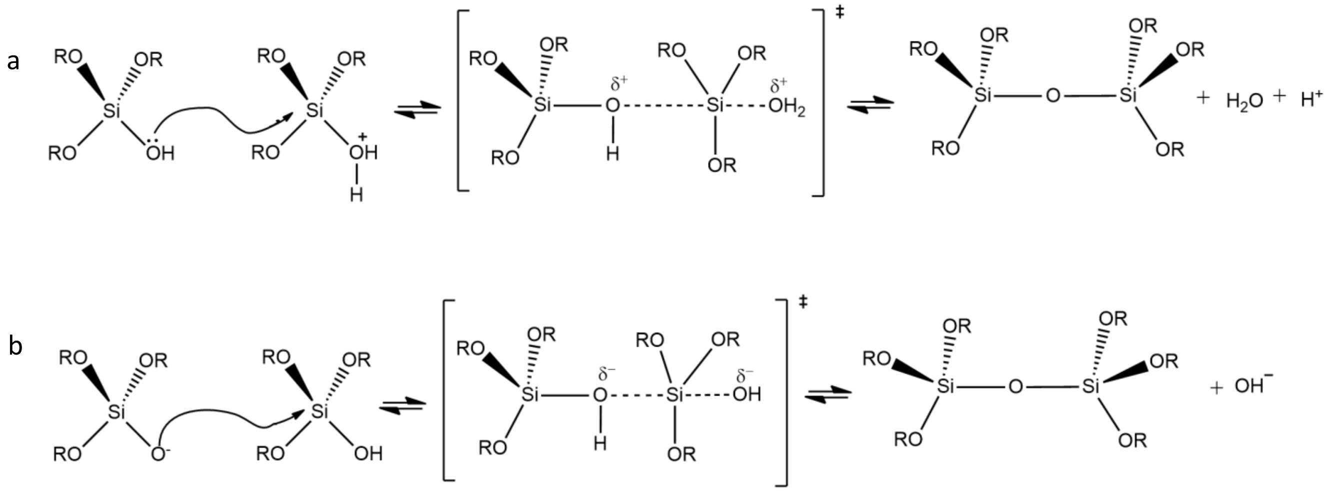

Figure 2.4 Mechanism of (a) Acid catalysed condensation of silicon alkoxides and (b) Base catalysed condensation of silicon alkoxides.

Although the hydrolysis and condensation reactions have been described as consecutive, they actually compete with each other during all steps of the sol-gel process. Furthermore, the rates of these reactions have an inverse dependence on pH, which is reflected in the kinetics and thus in the final gel structure [16]. Considering that the PZC of silica is around pH 4.5, condensation is the rate determining step at pH <5 leading to the formation of numerous monomers or small oligomers with reactive Si-OH groups. Conversely, hydrolysis is the rate-determining step at pH >5 which leads to the prompt consumption of the hydrolysed species. Connected to this, there is the profound and fascinating difference in the structure of the silica gel as a result of the type of catalysis adopted, Figure 2.5. Under acidic conditions, driven by inductive effects, the reaction proceeds mainly at the extremities of the chains where unreacted -OR groups are able to stabilise the positively charged transition state to a greater extent. Conversely, the reactions proceed preferentially on the silicon atoms at the centre of the growing chain when a base is adopted.

More branched (i.e. more highly condensed) networks are thus attained with the basic conditions whereas chain-like networks result under acidic conditions. The type of catalyst results to be one of the key factors to tailor the porosity and the structure-adsorption characteristics in final materials: use of a basic catalyst results in a larger amount of mesopores in the final material while an acidic catalyst shifts porosity towards microporosity [17, 18].

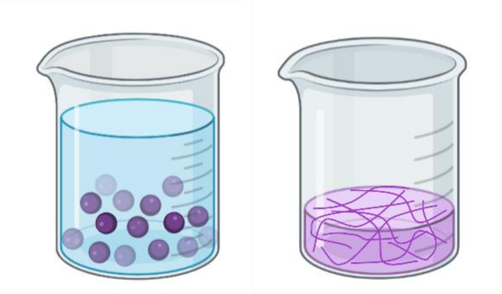

Figure 2.5 Silica gel structure from basic (left) and acid (right) condition

2.3 Metal alkoxide

The greater electropositive character of transition metals compared to silicon, together with the ability to expand their coordination sphere beyond 4, makes transition metal alkoxides more prone to nucleophilic attack than silicon alkoxides. Thus, the big issue when the preparation involves the transition metal alkoxides is their very fast reaction with water that leads to precipitation instead of a homogeneous sol, with poor control on composition and homogeneity. For example, the hydrolysis rate of $Ti(OR)_4$ is about 10^5 higher than the corresponding $Si(OR)_4$ under the same conditions [19]. A further consequence of the pronounced Lewis acidity of metals in alkoxides is the inclination of metal alkoxides to associate via OR bridges or to coordinate alcohol molecules [20]. On the other side, silicon alkoxides are present in solution as monomeric forms. It is clear that the reactivity of transition metal alkoxides, besides the inductive and steric size factors already discussed for silicon precursors, can also be traced back to the possible degree of oligomerisation. $Ti(OEt)_4$, for example, is more reactive than $Ti(OiPr)_4$ because the former in alcohol is present as a trimeric structure while the latter as a monomer in isopropanolic solution. Metal size can also increase the tendency to form complex structures.

If the goal of the research is to take a step forward in the rational design of catalysts based on transition metal oxides, an understanding of the unexpected chemistry of such precursors is required.

Just a short while ago, in March 2022, Ulrich Schubert reported interesting findings from his own research focused on the in-depth inspection of clusters formation in "sol" prepared starting from transition metal alkoxides. The study sheds light on the oligomeric structures, $[M(OR)_m]_n$, present in the first step of gel formation [21].

Another important aspect that should not be surprising considering the different chemistry of the two families of alkoxides considered so far is the final gel structure. Silicon is in fact tetrahedrally coordinated to oxygen and the interconnected Si tetrahedra only share corners rather than edges or faces while metals have usually an octahedral coordination and less degree of freedom of the polyhedra to reach the final stoichiometry MO_2 [21]. Semi or microcrystalline oxides are obtained by sol-gel processing of transition metal precursors whereas silica gel retains its amorphous nature.

The reactivity of the transition metal alkoxides is to some extent moderated with the use of complexing ligands which are commonly -diketones, polyhydroxy acids, or carboxylic acids. The chelating action, by blocking an additional coordination site, increases the metal coordination number and decreasing the number of easily hydrolysable groups. The bi- or (tri-)dentate ligands can also bridge two metal atoms in dimeric structures [20]. These modified precursors have consequence on reaction pathway and thus on the microstructure and texture of the obtained gels.

In recent times, the study of the formation of metal oxo clusters has gained even more prominence not only in the specific field of sol-gel but also because they are considered to be the core of MOFs, heterogeneous catalysts with extremely high potential [22].

From the above, it is evident that the gel obtained is the result of a delicate balance among the many factors involved since many different pathways from the molecular precursor to the final gel are possible. This should by no means be underestimated if rational catalyst design is to be done.

Other parameters that influence the rate of the hydrolysis and condensation reaction include pH, temperature, and reaction time, the concentration of reagents, the type and concentration of surfactant or structure directing agents and $H_2O/M(OR)_4$ molar ratio.

A detailed understanding of the parameters influencing the reaction rates and thus the structure evolution is necessary in order to tailor the texture and properties of sol–gel materials.

References

1. J.J. Ebelmen, Untersuchungen über die verbindung der barsaure und kieselsaure mit aether. Ann. Chim. Phys. Ser. 1846, 57, 319–355.
2. T. Graham, On the properties of silicic acid and other analogous substances. J. Chem. Soc. 1864, 17, 318–327.
3. C.B. Hurd, Theories for the mechanism of the setting of silicic acid gels. Chem. Rev. 1938, 22, 403–422.
4. S. Sakka History of the Sol-Gel Chemistry and Technology in Handbook of Sol-Gel Science and Technology Processing, Characterization and Applications. Editors: Lisa Klein, Mario Aparicio, Andrei Jitianu https://doi.org/10.1007/978-3-319-32101-1
5. L.L. Hench, J.K. West, The sol-gel process. Chem. Rev. 1990, 90, 33–72.
6. R.J. Hook, A ^{29}Si NMR study of the sol-gel polymerisation rates of substituted ethoxysilanes. J. Non-Cryst. Solids 1996, 195, 1–15.
7. R.J.P. Corriu, D. Leclercq, Recent Developments of Molecular Chemistry for Sol–Gel Processes. Angew. Chem. Int. Ed. Engl. 1996, 35, 1420-1436. https://doi.org/10.1002/anie.199614201.
8. J. Livage, C. Sanchez, Sol-gel chemistry. Journal of Non-Crystalline Solids Volume 145, 1992, Pages 11-19.
9. C.J. Brinker, G. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, 1st ed.; Academic Press Inc: New York, NY, USA, 1990.
10. J. Livage, Inorganic Materials, Sol–Gel Synthesis of. Encyclopedia of Materials: Science and Technology (Second Edition) 2001, Pages 4105-4107.
11. E.J.A. Pope, J.D. Mackenzie Sol-gel Processing of Silica: II. The role of the catalyst. J. Non Cryst. Solids 1986, 87, 185-198. https://doi.org/10.1016/S0022-3093(86)80078-3
12. A. E. Danks, S. R. Hall, Z. Schnepp, The evolution of 'sol–gel' chemistry as a technique for materials synthesis. Mater. Horiz. 2016,3, 91.
13. U. Schubert, New materials by sol–gel processing: design at the molecular level. J. Chem. Soc., Dalton Trans., 1996, 3343-3348.
14. R. Ciriminna, A. Fidalgo, V. Pandarus, F. Béland, L. M. Ilharco, M. Pagliaro, The Sol−Gel Route to Advanced Silica-Based Materials and Recent Applications. Chem. Rev. 2013, 113, 6592−6620. dx.doi.org/10.1021/cr300399c
15. M. Pagliaro, Sol–gel catalysts for synthetic organic chemistry: milestones in 30 years of successful innovation. J. Sol-Gel Sci. Technol. 2020, 95, 551–561. https://doi.org/10.1007/s10971-020-05266-3.
16. H. Li, X. Chen, D. Shen, F. Wu, R. Pleixats, J. Pan, Functionalized silica nanoparticles: classification, synthetic approaches and recent advances in adsorption applications. Nanoscale, 2021,13, 15998–16016.
17. S. Esposito, "Traditional" Sol-Gel Chemistry as a Powerful Tool for the Preparation of Supported Metal and Metal Oxide Catalysts. Materials 2019, 12, 668; doi:10.3390/ma12040668.
18. A.F. Sierra-Salazar, A. Ayral, T. Chave, V. Hulea, S.I. Nikitenko, S. Abate, S. Perathoner, P. Lacroix-Desmazes, Chapter 18 - Unconventional Pathways for Designing Silica-Supported Pt and Pd Catalysts with Hierarchical Porosity Studies in Surface Science and Catalysis 2019, 178, 377-397. https://doi.org/10.1016/B978-0-444-64127-4.00018-5.
19. X. Lu, K. Kanamori, K. Nakanishi, Hierarchically porous monoliths based on low-valence transition metal (Cu, Co, Mn) oxides: gelation and phase separation. National Science Review 2020, 7, 1656–1666. doi: 10.1093/nsr/nwaa103.
20. U. Schubert, Organically Modified Transition Metal Alkoxides: Chemical Problems and Structural Issues on the Way to Materials Syntheses. Acc. Chem. Res. 2007, 40, 730–737.

21. U. Schubert, En route from metal alkoxides to metal oxides: metal oxo/alkoxo clusters. J. Sol-Gel Sci. Technol. 2022 https://doi.org/10.1007/s10971-022-05774-4.
22. V. Pascanu, G.G. Miera, A.K. Inge, B. Martín-Matute. Metal–Organic Frameworks as Catalysts for Organic Synthesis: A Critical Perspective. J. Am. Chem. Soc. 2019, 141, 7223–7234. DOI: 10.1021/jacs.9b00733.