

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

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Abstract This paper summarizes recent literature data and presents new experimental data on the mechanisms of chemical modification, hydrolysis and polycondensation of the alkoxides and demonstrates possibilities to approach new classes of materials, exploiting these mechanisms. Low reactivity of silicon alkoxides is improved by either basic catalysis exploiting an S_N2 mechanism or acidic catalysis facilitating a proton-assisted S_N1 mechanism as well as by modification with chelating ligands. Metal alkoxides are much stronger Lewis bases compared to silicon alkoxides and the acidity of water is strong enough to achieve their rapid hydrolysis via proton-assisted S_N1 pathway even in the absence of additional catalysts. Introduction of the modifying chelating ligands is leading generally to increased charge distribution in the precursor molecules. Modifying chelating ligands are also appreciably smaller than the alkoxide ligands they replace. The modification with chelating ligands is thus facilitating the kinetics of hydrolysis and polycondensation. The size and shape of the primary particles formed in sol-gel treatment of metal alkoxides are defined not by kinetic factors in their hydrolysis and polycondensation but by

the interactions on the phase boundary, which is in its turn directed by the ligand properties. The products of the fast hydrolysis and condensation sequence consist of micelles templated by self-assembly of ligands (mainly oxo-species). This concept provides explanations for commonly observed material properties and allows for the development of new strategies for the preparation of materials. We discuss the formation of inverted micelles, obtained by the appropriate choice of solvents, which allows for the formation of hollow spheres. The modifying β -diketonate ligands act as the surfactant and form an interface between the hollow sphere and the solvent. Retention of ligands inside the gel particles is possible only if ligands possessing both chelating and bridging properties are applied. Application of such ligands, for example, diethanolamine, permits to prepare new transition metal oxide based microporous membranes.

Keywords Sol-gel · Chemical modification · Gelation mechanism · Micelle templated by self-assembly of ligands (MTSAL) · Hollow spheres · Microporous membrane

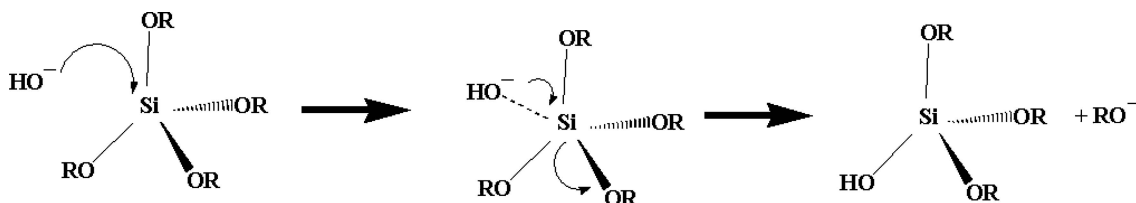
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Introduction

Sol-gel is an attractive synthetic approach to metal oxide materials applied in a wide variety of fields including structural ceramics [1, 2], sensors [3–5], catalysts [6, 7], optics [8, 9] and electronics [10, 11]. Despite being widely applied, the chemistry of the sol-gel synthesis utilizing metal alkoxide precursors is hardly understood. The generally assumed concepts for the sol-gel chemistry of main group and transition metal oxides are derived from early studies on silica.



Scheme 1

Sol-gel chemistry of silica

The formation of a sol particle is initiated upon the addition or release of water. The water initiates the hydrolysis and subsequent condensation reactions [e.g., 12, 13]. Common silicon alkoxides, the alkoxy silanes, are, however, essentially stable to hydrolysis by water in the absence of catalysts. Catalysts applied in hydrolysis of alkoxy silanes are protolytes, acids or bases.

The hydrolysis of a silicon alkoxide leads to the formation of a reactive Si-OH group. The following three-step S_N2 mechanism is generally proposed for the base-catalyzed reaction: The first step is a nucleophilic addition of a hydroxide anion to the positively charged Si atom. This leads to a transition state, where the coordination number of Si has been increased by one. The second step involves a charge transfer within the intermediate state leading to release of an alkoxide anion, which in its turn reacts with water regenerating the hydroxide catalyst. This S_N2 mechanism is summarized in Scheme 1.

The kinetics of nucleophilic substitution is governed by the charge distribution. The reaction is strongly favored when the nucleophilic character of the entering group and the electrophilic strength of the central atom are high. Both the positive charge of the central atom and the negative charges of the alkoxide oxygen atoms are rather low for tetracoordinated silicon compounds because of strong $p\pi - d\pi$ interactions (charge compensation via increased bond multiplicity). The basic catalysis for silicon alkoxides, following the S_N2 mechanism, is thus a relatively slow reaction.

The acidic catalysis exploits a different reaction pathway. Addition of acids leads at the first step to the protonation of an oxygen atom in the alkoxide ligand, leading to formation of the reactive cationic species (see Scheme 2). This step is rate-determining, which results in an S_N1 -type mechanism.

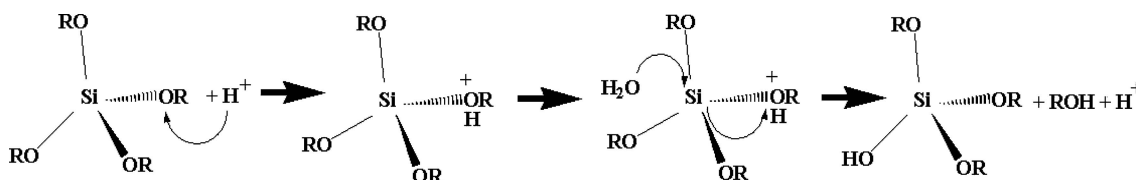
The cation thus formed is attacked by a water molecule, which leads again to formation of a Si-OH bond, release of an alcohol molecule (better leaving group) and regeneration of a proton catalyst.

Acidic catalysis results in much quicker hydrolysis than the basic one at the same concentration of a protolytic catalyst, indicating that silicon alkoxides are stronger Lewis bases than Lewis acids.

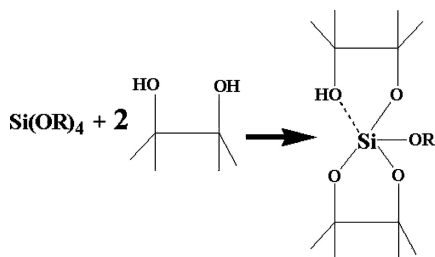
After the initial hydrolysis, the product can react further either *via* another hydrolysis reaction or a condensation reaction. In order to get less branched oligomers, the hydrolysis should be followed by a condensation reaction. Condensation is a complex process and, depending on the experimental conditions, three competitive mechanisms have to be considered: alcoxolation, oxolation and olation [e.g., 12, 13].

Alcoxolation is a reaction by which a bridging oxo group is formed through elimination of an alcohol molecule. The mechanism is basically the same as for hydrolysis with Si replacing H in the entering group. Oxolation follows the same mechanism as alcoxolation, but a water molecule is the leaving group. Olation can occur when full coordination of Si is not achieved. In this case, bridging hydroxo groups can be formed through elimination of a solvent molecule. The latter can be either H_2O or ROH depending on the water concentration in the medium. All these reactions are catalyzed by protons, i.e. acidic medium, and are slowed down in the presence of bases.

The chemistry of modification of the silicon alkoxides with chelating ligands has been developed quite recently, mainly during the last decade and was driven by the interest to the structure and reactivity of highly coordinated silicon centers. It has been shown that interaction of silicon alkoxides or chlorides with glycols results in pentacoordinated species [14, 15], see Scheme 3. Their most prominent features are the increased reactivity in exchange of



Scheme 2

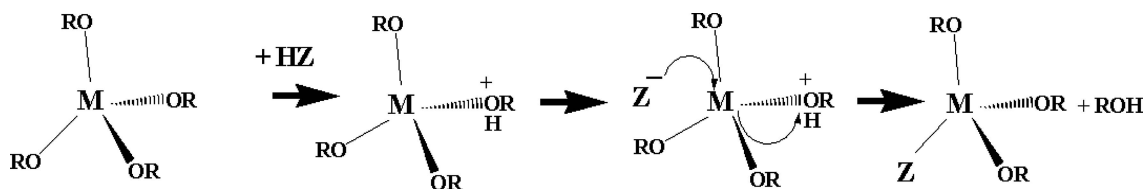


Scheme 3

alkoxide ligands, compared to tetracoordinated silicon alkoxides [15].

The pentacoordinate anions, formed in the presence of bases, possess strongly improved Lewis basicity and are demonstrating much easier exchange for the alkoxide group than non-modified silicon alkoxides [16], apparently via facilitated action of a proton-assisted $\text{S}_{\text{N}}1$ -type reaction mechanism. Facile reactivity of silicon alkoxides modified by diols in the absence of catalysts has recently been successfully applied by Nicola Hüsing for the synthesis of materials with hierarchical porosity [17]. This work has been awarded by the Donald Ulrich International Award in 2005. The same trend in the development of reactivity has recently been observed even for the modification of silicon alkoxides with β -diketones: the resulting hexacoordinate bis- β -diketoalkoxides, e.g., $\text{Si}(\text{thd})_2(\text{OR})_2$, are rather water sensitive in contrast to non-modified $\text{Si}(\text{OR})_4$ [18]. The chemical modification by chelating ligands has thus been documented to strongly facilitate hydrolysis and polycondensation of silicon alkoxides.

The particle size, morphology and porosity of silica-based materials are generally considered as governed by the kinetic factors of the hydrolysis-polycondensation process [12, 13]. A specific phase organization, necessary for creation of organized pore systems has been until quite recently considered accessible only via introduction of surfactants [17]. It has now been observed, however, that the interaction between ligands and solvent can dominate over the kinetic factors and be directing for the formation of sol particles for sol-gel of silicon alkoxides. For example, core-shell structures have been obtained by sol-gel treatment of alkyl-trialkoxysilanes in an oil-in-water emulsion in the absence of surfactants [19].



Scheme 4

Sol-gel chemistry of main group and transition metal oxides

The major difference in reactivity of metal alkoxides from those of silicon lies in their very facile and rapid reaction with water in the absence of catalysts. The reaction times for hydrolysis of titanium alkoxides have order of magnitude of milliseconds and zirconium alkoxides—microseconds [20], i.e. 10^5 – 10^8 times quicker than silicon alkoxides [21]. Major difference in the chemistry of metals in general, both main group and transition ones, from that of non-metals or semimetals, such as silicon, lies in their ability to easily form relatively stable cationic complexes. This feature in combination with well-acknowledged high Lewis basicity of metal alkoxides (broadly applied as Lewis base catalysts in various reactions in organic chemistry, e.g. the lactone polymerization [22]) facilitates the ligand exchange through proton-assisted $\text{S}_{\text{N}}1$ reaction mechanism. According to the experimental kinetic measurements, the ligand exchange, i.e. both hydrolysis and chemical modification, start with the protonation of a negatively charged alkoxide oxygen atom [23]. The generated reactive cationic species coordinates then an additional donor ligand and releases an alcohol molecule, see Scheme 4.

It should be noted that the reaction speed is determined in the first hand by the acidity of the HZ reactant, while the nucleophilic properties of the entering Z^- ligand have no influence on the ligand exchange process [24]. Recent studies of the complex formation between titanium or zirconium alkoxides and amine ligands have shown that even in this case the ligand electron donor properties play minor if any role at all—the most stable complexes were observed in fact for the amines displaying highest Brönsted acidity, i.e. those able to form a stable hydrogen bond (protonate) an alkoxide oxygen atom [25].

The theoretical impossibility of an alternative $\text{S}_{\text{N}}2$ mechanism, often proposed earlier for the explanation of higher reactivity of metal alkoxides [26], has recently been clearly demonstrated by the work of Henry et al. [27]. Calculated activation energies for the replacement of an alkoxide ligand via $\text{S}_{\text{N}}2$ mechanism turned to have the order of magnitude of about 600 kJ/mol, while the experimentally determined values are 20–30 kJ/mol (20 times lower!) [23], being consistent only with the proton-assisted $\text{S}_{\text{N}}1$ mechanism.

High reactivity of the chemically unmodified metal alkoxides towards water results most often in massive uncontrolled phase separation, “precipitation”, on hydrolysis of their solutions by pure water or its solutions in organic solvents. Ram Mehrotra pioneered in the early 1970-es the studies of chemical modification of alkoxides with different acidic ligands such as carboxylic acids, β -diketones, functional alcohols etc. [28]. It has been noted that addition of water to solutions of modified alkoxides resulted often in formation of clear sols and not precipitates. In the lack of direct evidence it has been concluded that introduction of modifying, most often—chelating, ligands decreased the reactivity of precursors in hydrolysis and polycondensation reactions [29]. The proposed explanation was that the introduction of chelating ligands is: (1) *not changing significantly the charge distribution in the molecules*, (2) *blocking the coordination sites of the metal atoms*, and (3) *shielding the metal atoms from polycondensation by non-hydrolysable and thus not removable ligands* [29]. This explanation has been reproduced in the recent books on the topic such as the “Synthesis of Inorganic Materials” by U. Schubert and N. Hüsing [21] and “The Chemistry of Metal Alkoxides”, by N. Turova et al. (in the Chapter 7, “Heteroleptic Metal Alkoxide Complexes” by V. Kessler) [30]. In the view of the data already available on reaction mechanism for metal alkoxides and on its transformation for silicon alkoxides on chemical modification, this explanation does not appear realistic. The aim of the present paper is to show that all of the abovementioned three postulates are wrong, i.e. hydrolysis and polycondensation of metal alkoxides are, in analogy with silicon alkoxides, facilitated by the chemical modification and their kinetics has no direct relation to the sol-gel transformation of metal alkoxides.

Experimental

All manipulations were carried out in a dry nitrogen atmosphere using Schlenk technique or a glove box. Water free $\text{Ni}(\text{acac})_2$ was obtained by sublimation of $\text{Ni}(\text{acac})_2 \cdot x\text{H}_2\text{O}$ (Aldrich Chemical Company Inc.) at 150–170°C and 0.1 mm Hg. Strontium metal, titanium ethoxide, zirconium isopropoxide, $[\text{Zr}(\text{O}^i\text{Pr})_4(^i\text{PrOH})_2]$ 99.9%, and 70 wt% solution of Zr (O^nPr)₄ were purchased from Aldrich. Isopropanol and *n*-propanol (Merck, p.a.) were purified by distillation over corresponding $\text{Al}(\text{OPr})_3$, and hexane and toluene (Merck, p.a.)—by distillation over LiAlH_4 . Acetylacetonate, Hacac, and tetramethylheptanedion, Hthd, were purchased from Aldrich and used without further purification. IR spectra of nujol mulls were registered with a Perkin Elmer FT-IR spectrometer 1720 X. Mass-spectra were recorded using JEOL JMS-SX/SX-102A mass-spectrometer applying

electron beam ionization ($U = 70$ eV) with direct probe introduction. Bimetallic strontium-zirconium isopropoxide β -diketonate, $\text{Sr}_2\text{Zr}_2(\text{thd})_4(\text{O}^i\text{Pr})_8$, was obtained according to the earlier described technique [31]. The charge distribution calculations were carried out applying the model developed by M. Henry et al. described in [27].

$\text{Sr}_2\text{Zr}(\text{thd})_4(\text{O}^i\text{Pr})_4(^i\text{PrOH})$ (1)

1.99 g of the $\text{Sr}_2\text{Zr}_2(\text{thd})_4(\text{O}^i\text{Pr})_8$ complex were dissolved on reflux in a mixture of 2 ml toluene and 3 ml hexane. 2 ml $^i\text{PrOH}$ were added by syringe to the clear solution cooled to room temperature. The solvent was then evaporated to dryness leaving viscous syrup that was redissolved in 3 ml hexane and left for crystallization at room temperature. A crop of big (majority over 1 mm) colorless prismatic crystals precipitated after several days and were separated by decantation and dried in vacuum at room temperature. The exact composition was confirmed by X-ray single crystal study. Yield 0.76 g (46%). Found, %: C 53.77; H 8.4. Calculated for $\text{C}_{59}\text{H}_{112}\text{O}_{13}\text{Sr}_2\text{Zr}$, %: C 54.68; H 8.64. IR, cm^{-1} : 3610 s, 3420 w, 3390 w, 1590 s, 1576 s, 1560 s, 1541 m, 1509 s, 1412 m, 1360 sh, 1297 w, 1246 w, 1225 m, 1170 m, 1145 m, 1121 s, 1015 s, 968 s, 954 s, 870 m, 852 w, 821 w, 797 m, 770 w, 752 w, 620 m, 570 m, 536 m, 470 s, 450 sh. M-S, $m/z(\%)$, interpretation ($\text{P} = \text{Sr}_2\text{Zr}(\text{thd})_4(\text{O}^i\text{Pr})_4(^i\text{PrOH}) +$, parent ion): 1234(3), $[\text{P}-\text{ROH}]^+$, 1219(4), $[\text{P}-\text{ROH}-\text{CH}_3]^+$, 1175(38), $[\text{P}-\text{ROH}-\text{OR}]^+$, 1116(56), $[\text{P}-\text{ROH}-2\text{OR}]^+$, 1091(17), $[\text{P}-\text{ROH}-2\text{OR}-\text{CH}_3]^+$, 1051(57), $[\text{P}-\text{ROH}-\text{thd}]^+$, 992(100), $[\text{P}-\text{ROH}-\text{OR}-\text{thd}]^+$, 949(6), $[\text{P}-\text{ROH}-\text{thd}-\text{R}_2\text{O}]^+$, 933(5), $[\text{P}-\text{ROH}-2\text{OR}-\text{thd}]^+$, 868(3), $[\text{P}-\text{ROH}-2\text{thd}]^+$.

$\text{Ni}_2\text{Ti}_2(\text{acac})_4(\text{OEt})_8$ (2)

Anhydrous $\text{Ni}(\text{acac})_2$ (4.08 g, 16 mmol) and $\text{Ti}(\text{OEt})_4$ (3.3 ml, ~ 16 mmol) were dissolved on short reflux in 15 ml toluene and left for crystallization overnight at room temperature. The formed prismatic emerald green crystals were separated by decantation and dried in vacuum. The exact composition was confirmed by an X-ray single crystal study. Yield 6.61 g (86%). Found, %: C 44.10; H 7.0. Calculated for $\text{C}_{36}\text{H}_{68}\text{O}_{16}\text{Ti}_2\text{Ni}_2$, %: C 44.57, H 7.1. IR, cm^{-1} : 1595 s, 1519 s, 1283 w, 1256 w, 1187 w, 1161 w, 1112 m, 1071 m, 1031 m, 921 m, 778 m, 762 m, 659 m, 576 s, 550 s, 521 s, 454 sh. M-S, $m/z(\%)$, interpretation: 291(27), $\text{Ti}(\text{acac})_2(\text{OR})^+$, 256 (100), $\text{Ni}(\text{acac})_2^+$, 241(100), $[\text{Ni}(\text{acac})_2-\text{CH}_3]^+$, 183(64), $\text{Ti}(\text{OEt})_3^+$, 157(100), $\text{Ni}(\text{acac})^+$. Solubility of **2** in toluene is about 3 g per 100 ml at 20°C, but is very strongly increased on heating.

Table 1 Crystal data and the diffraction experiments details for compounds **1–3**

	1	2	3
Chemical composition	C ₅₉ H ₁₁₂ O ₁₃ Sr ₂ Zr	C ₃₆ H ₆₈ O ₁₆ Ti ₂ Ni ₂	C ₄₂ H ₇₂ O ₁₉ TiNi ₅
Formula weight	1295.95	970.12	1222.45
Crystal system	Monoclinic	Monoclinic	Hexagonal
Space group	<i>P2(1)/c</i>	<i>P2(1)/n</i>	<i>R-3</i>
μ/mm^{-1}	1.622	1.132	1.877
<i>a</i> /Å	25.34(3)	11.995(8)	20.26(2)
<i>b</i> /Å	16.407(12)	14.664(10)	20.26(2)
<i>c</i> /Å	17.812(16)	14.907(19)	11.623(14)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	90.12(7)	111.246(12)	90
$\gamma/^\circ$	90	90	120
<i>V</i> /Å ³	7406(12)	2444(3)	4133(8)
<i>T</i> /K	295(2)	295(2)	295(2)
<i>Z</i>	4	2	3
Number of independent reflections	5528 [<i>R</i> _{int} = 0.0701]	2446 [<i>R</i> _{int} = 0.0543]	833 [<i>R</i> _{int} = 0.0816]
Number of observed reflections	3097 [<i>I</i> > 2σ(<i>I</i>)]	1391 [<i>I</i> > 2σ(<i>I</i>)]	553 [<i>I</i> > 2σ(<i>I</i>)]
<i>R</i> ₁	0.0926	0.0528	0.0739
<i>wR</i> ₂	0.2512	0.1186	0.1843

Ni₅TiO(acac)₆(OEt)₆ (**3**)

Compound **2** (0.76 g, about 0.8 mmol) was dissolved in 2 ml anhydrous toluene on short heating to about 50°C and the solution was cooled to room temperature. 3 ml 99.5% EtOH was added then to the reaction mixture. Precipitation of light green needle-shaped crystals occurred within a couple of minutes. Yield 0.37 g (practically quantitative). Found, %: C 41.36; H 6.0. Calculated for C₃₆H₆₈O₁₆Ti₂Ni₂, %: C 41.27, H 5.9. IR, cm⁻¹: 1600 s, 1516 s, 1255 w, 1187 w, 1161 w, 1112 m, 1071 m, 1031 m, 921 m, 778 m, 762 m, 665 m, 576 s, 545 s, 440 sh. M-S, m/z(%), interpretation: 291(2), Ti(acac)₂(OR)⁺, 256 (87), Ni(acac)₂⁺, 241(96), [Ni(acac)₂ – CH₃]⁺, 183(19), Ti(OEt)₃⁺, 157(100), Ni(acac)⁺. Compound **3** is practically insoluble in organic solvents. Big single crystals of **3** were obtained by refluxing a solution of **2** in a mixture of toluene and isopropanol.

Crystallography

The data collection for all the single crystals of compounds **1–3** studied was carried out at 22°C on a SMART CCD 1k diffractometer with graphite monochromated MoK_α radiation (for details see Table 1). All the structures were solved by direct methods. The coordinates of the metal atoms were obtained from the initial solutions and for all other non-hydrogen atoms found in subsequent difference Fourier syntheses. The structures were refined by least squares first in isotropic and then in anisotropic approximations (except for carbon atoms with occupational disorder in **1** (solvating isopropanol and bridging thd ligand) and in **3** (all carbon atoms), which were refined only isotropically). The coordinates of

the hydrogen atoms were calculated geometrically (except for compound **3** where their location is impossible because of disorder problems) and were included into the final refinement in isotropic approximation for compounds **1** and **2**. All calculations were performed using the SHELXTL-NT program package [32] on an IBM PC.

Calorimetric measurements

The precursor, Zirconium-*n*-propoxide (70% (wt) in 1-propanol, Aldrich) was mixed with 1-propanol (99.7% anhydrous, Aldrich) in a 1/10 molar ratio. Stabilizers acetylacetone (pro analyze, Merck), triethanolamine (pro analyze, Merck), or glacial acetic acid (100%, Merck) was added with a precursor/stabilizer molar ratio of 1:2. Finally, 2 equivalent mol of water was added to 30 grams of stabilized precursor using a syringe. During the addition of the stabilizers and water the temperature was monitored and by temperature indicator (using the temperature probe of a Brookfield DV-2 Digital Viscometer) and the data stored in a computer.

After adding the stabilizer the solutions had a pH between 4.5 and 6. Immediately after addition of the stabilizer an apparent increase in temperature is noticeable. This change in temperature can be attributed to heat evolving from exothermic ligand exchange and heat evolving from mixing and other chemical reactions. The latter effects were studied by repeating the experiments without the precursor. The temperature change not related to ligand exchange appeared to be endothermic for acetone acetyl ($\Delta T \sim -5^\circ\text{C}$), while for acetic acid and triethanolamine the effect was only minor. After a crude correction the temperature change associated

with ligand exchange appears to follow: acetylacetonate > triethanolamine > acetic acid. In all cases, after the initial increase an exponential decrease in temperature is observed. Such behavior is expected for cooling due to a temperature difference with the surroundings.

The stabilizing effect of different additives is compared by the addition of 2 equivalent mol of water to zirconium precursor. The added water causes hydrolysis of the (stabilized) precursor, which is a fast exothermic reaction. The evolution temperature with time, upon addition of water, is depicted in the figure. For all cases the temperature increases after water has been added. An especially fast and large increase in temperature is observed for the acetylacetonate and triethanolamine stabilized precursors. The magnitude of the absolute temperature rise follows the series acetylacetonate > triethanolamine > acetic acid > unstabilized precursor. The visually estimated extent of stability (i.e., absence of precipitate formation) follows almost the same order, i.e. triethanolamine > acetylacetonate >> acetic acid > non-stabilized precursor.

For the non-stabilized and acetic acid stabilized systems immediate precipitation is observed when water is added. In the case of acetylacetonate some precipitation is observed one hour after addition of water, while for the triethanolamine system no precipitation was visible after 100 h. For non-stabilized precursor the rapid precipitation is not surprising, since the uncontrolled addition of water causes a locally excess of water. Subsequently, hydrolysis and condensation occur rapidly leading to an almost instantaneous precipitation.

Sol preparation and characterization and film deposition

The inverted micelles are typically obtained when a small amount of polar solvent is introduced into a non-polar one and the droplets of the former are stabilized by a surfactant. The macro-droplets of emulsions were obtained by introduction of water solutions into hexane solutions of $Zr(O^iPr)_3(thd)$ (typically 0.2 g in 5 ml hexane) on vigorous shaking. Nano-droplets were obtained using isopropanol as co-surfactant. The introduction of water solution in iso-

propanol (1:20 volume ratio) into larger volume of hexane results in a clear emulsion. Thus, when the water-propanol solution is quickly added by a syringe to a 0.3–1.0 molar hexane solution of modified precursor (the metal to water ratio was maintained around 1), a clear sol is obtained. The detailed composition of the prepared samples is summarized in Table 2.

The samples for light scattering and TEM experiments were prepared from the dried sols that were re-dissolved in ~20 ml of parent alcohol. The samples were ultrasonically treated for 15 min. The particle size of the clear solution was determined by light scattering. For TEM analysis a drop of the solution was deposited on a copper supported carbon grid.

Particle size in the obtained sols was determined using light scattering technique with a Zetasizer 3000HS instrument. Transmission Electron Microscopy (TEM) images were obtained with PHILIPS CM30 Twin/STEM instrument. The formed single crystals were identified by determination of their unit cell parameters. Scanning Electron Microscopy images (SEM) were registered on LEO Gemini 1550 FEG-SEM instrument.

Optical microscopy

The biological encapsulates within hydrated metal oxide spheres were studied using an Axiophot epifluorescence microscope (Zeiss, Oberkochen, Germany) with an excitation filter at 485 nm (band pass 20 nm) and emission wavelengths >520 nm. For photographs, images were obtained using a 20 × or 100 × oil immersion objective.

Results and discussion

The aim of the present work is to demonstrate that the chemical modification is not slowing down the hydrolysis and polycondensation reactions, providing in the first hand experimental and also theoretical evidence for inconsistency of the arguments supporting the opposite point of view. We

Table 2 Conditions of sol preparation in inverted micellar systems

Sample name	Precursor	Modifier	Ratio Zr:H ₂ O	Concentration		Remark
				Zirconium [mol l]	Hexane: propanol	
HS1	$[Zr(O^iPr)_3(acac)]_2$	–	1.04	1	2	
HS2	$[Zr(O^iPr)_3(acac)]_2$	–	1.1	0.98	2	aged precursor
HS3	$[Zr(O^iPr)_3(acac)]_2$	–	1.01	0.29	2	
HS4	$[Zr(O^iPr)_3(acac)]_2$	–	1	0.3	8.8	
HS5	$[Zr(O^iPr)_3(acac)]_2$	–	0.92	0.58	4.4	
HS7	$Ti(O^iPr)_4$	1 mol Hacac	1.03	0.3	2	
HS8	$Zr(O^iPr)_4$	1 mol Hacac	0.99	0.3	2	
HS9	$Zr(O^iPr)_4$	1 mol Hthd	1.02	0.3	2	

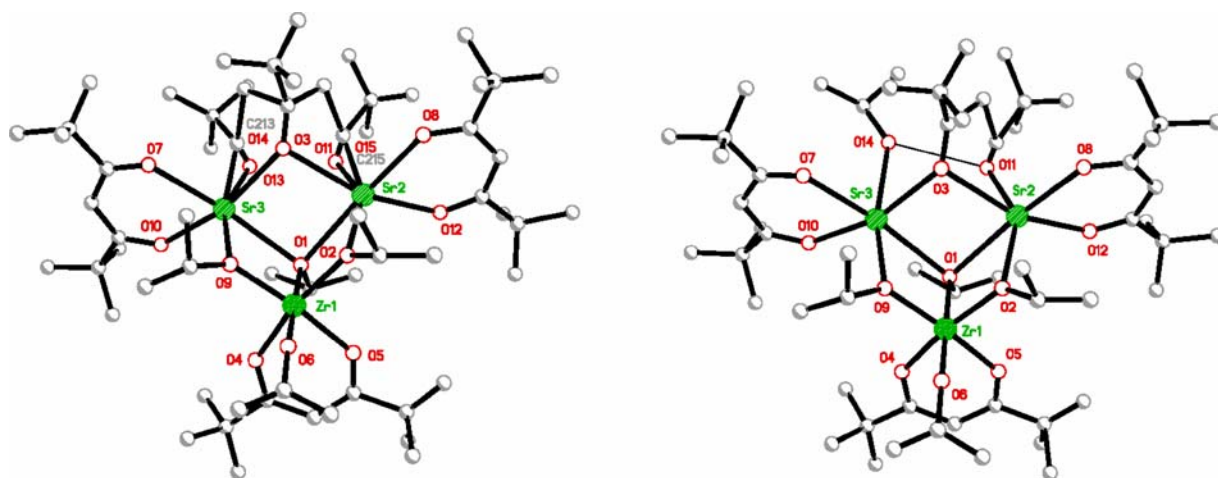


Fig. 1 Molecular structure of $\text{Sr}_2\text{Zr}(\text{thd})_4(\text{O}^i\text{Pr})_4(\text{}^i\text{PrOH})$ (**1**) showing true ligand disorder (a) and one of the two possible arrangements of real ligands (b). The thin line connecting O(11) and O(14) is showing the hydrogen bond between these atoms

would like also to demonstrate new application possibilities arising from this knowledge.

Chelating ligands are not blocking the coordination sites

It is currently assumed that such frequently applied bidentate chelating ligands as β -diketonate ones are more sterically demanding than two alkoxide groups they are replacing. In this paper we are providing for the first time direct crystallographic arguments against this assumption. Introduction of one β -diketonate ligand per metal atom most often does not change the coordination number. In the structure of compound $\text{Sr}_2\text{Zr}(\text{thd})_4(\text{O}^i\text{Pr})_4(\text{}^i\text{PrOH})$ (**1**) (Fig. 1(a) and (b)), a derivative containing “bulky” 2,2,6,6-tetramethylheptanedion (thd) ligands along with the isopropoxide ones, both strontium and zirconium atoms are hexacoordinated. The peculiar “ligand” bridging two strontium atoms in the Fig. 1(a) is a refinement model reflecting the statistics between a bridging thd ligand and a solvating alcohol molecule forming a short (2.50 Å) hydrogen bond to it as it is demonstrated in Fig. 1(b).

The possibility of crystallographic disorder is thus demonstrating that the “bulky” thd-ligand has in reality the same spatial requirements as a pair of isopropoxide ligands. The same coordination number 6 is observed for zirconium in both the isopropoxide, $\text{Zr}_2(\text{O}^i\text{Pr})_8(\text{}^i\text{PrOH})_2$ [31, 33], and the *n*-propoxide, $\text{Zr}_4(\text{O}^n\text{Pr})_{16}$ [34].

It is also interesting to follow the microhydrolysis of compound $\text{Ni}_2\text{Ti}_2(\text{acac})_4(\text{OEt})_8$ (**2**) (see Fig. 2), where the acetylacetonate ligands have different structural functions than the ethoxide ones, required to achieve the formation of a stable symmetric M_4O_{16} core (a fragment of hexagonal packing of metal and oxygen atoms). The introduction of water leads to complete change in the structure and com-

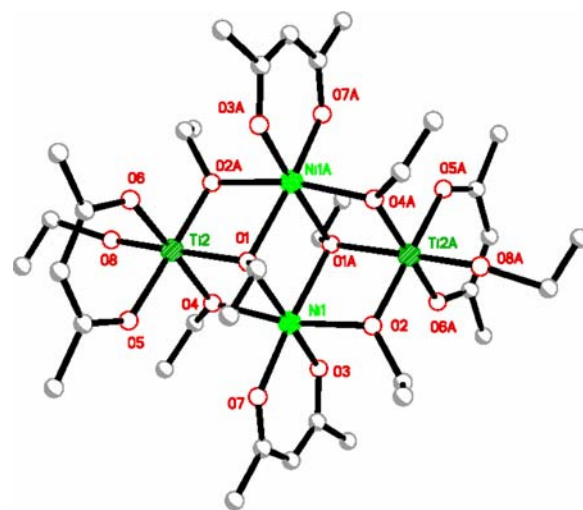


Fig. 2 Molecular structure of $\text{Ni}_2\text{Ti}_2(\text{acac})_4(\text{OEt})_8$ (**2**)

position yielding practically quantitatively the compound **3**, $\text{Ni}_5\text{TiO}(\text{acac})_6(\text{OEt})_6$.

The structure of compound **3** is highly symmetric (hexagonal) and involves 5 Ni and 1 Ti atom occupying uniformly each of the 6 positions in the M_6O_{19} hexametallate core (Fig. 3(a) and (b)). The solution of this structure discloses a high degree of crystallographic disorder with complete mixing of the ethoxide ligands and acac-ligands in the same positions (Fig. 3(a)).

The size and sterical requirements of the acac-ligands is thus equivalent to that of a pair of the ethoxide ligands. Modification with acetylacetonate is most commonly used for the isopropoxide derivatives of titanium, zirconium and aluminium alkoxides, which means that the entering ligand is much *smaller* than the isopropoxide or *n*-propoxide ligands it is replacing. The stability of the molecular structure of **3** and its extremely low solubility permit its formation even when

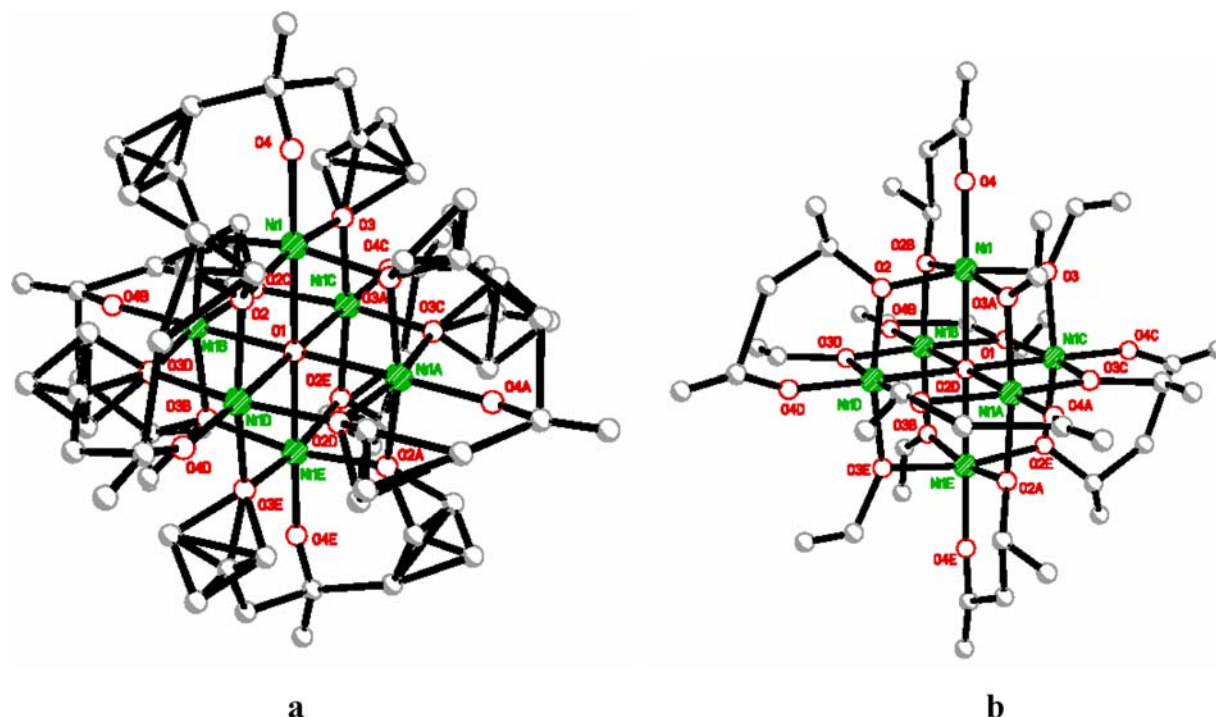


Fig. 3 Molecular structure of $\text{Ni}_5\text{TiO}(\text{acac})_6(\text{OEt})_6$ (**3**), showing true ligand disorder (a) and one of the two possible arrangements of real ligands (b)

the additional alcohol used for hydrolysis is isopropanol. The fact itself sounds extremely unusual, but is definitely compatible with the fact that the reactivity of metal alkoxides is practically exclusively a matter of thermodynamic control (in this case—the least soluble form precipitates) as we have earlier observed for a big number of studies of titanium, zirconium, aluminium, niobium, tantalum, molybdenum and tungsten alkoxides etc. [31, 35].

It can thus be concluded that the chelating ligands, being smaller than the alkoxide ones they replace, are not blocking the coordination sites at the metal atoms. It should also be mentioned, that blocking of the metal coordination sites can in general only play a minor role in the view of

the established proton-assisted $\text{S}_{\text{N}}1$ mechanism of alkoxides hydrolysis [23].

Chelating ligands are increasing the charge distribution

Information about charge distribution can on qualitative level easily be obtained from comparison of the bond lengths in the structures of the modified species and their non-modified analogues. One would expect that if the modifier would shorten the metal-oxygen bond length of an alkoxide ligand, it would reduce the reactivity of the alkoxide ligands towards hydrolysis. As it can be observed from our recently published data [31, 36–38] and the structure data available

Table 3 Metal-oxygen bond lengths (Å) in zirconium isopropoxide and Hacac, H_2dea , Hthd and tbaoc modified zirconium isopropoxide

Alkoxide ligand function	$[\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})_2]$ [30]	$[\text{Zr}(\text{O}^i\text{Pr})_3(\text{acac})_2]$ [35]	$\text{Zr}(\text{O}^i\text{Pr})(\text{acac})_3$ [35]	$[\text{Zr}(\text{O}^i\text{Pr})_3(\text{thd})_2]$ [36]
Bridging	2.171	2.258		2.219
Bridging	2.156	2.134		2.119
Terminal	1.936	1.955	1.922	1.944
Terminal	1.935	1.947		1.931
Terminal	2.079			
Alkoxide ligand function	$\text{Zr}(\text{O}^i\text{Pr})(\text{thd})_3$ [36, 38]	$\text{Zr}(\text{dea})_3(\text{Zr}(\text{O}^i\text{Pr})_3)_2$ ($^i\text{PrOH}$) ₂ [37]	$[\text{Zr}(\text{O}^i\text{Pr})_3(\text{tbaoc})_2]$ [39]	$\text{Zr}(\text{O}^i\text{Pr})_2(\text{tbaoc})_2$ [39]
Bridging			2.098	
Bridging			2.231	
Terminal	1.847	1.988	1.942	1.908
Terminal		1.927	1.922	1.908
Terminal		1.901		

Table 4 Metal-oxygen bond lengths (Å) in titanium isopropoxide and Hacac, Hthd and tbaoc modified titanium isopropoxide

Alkoxide ligand function	Ti(O ⁱ Pr) ₄ [40]	[Ti(O ⁱ Pr) ₃ (acac)] ₂ [41]	[Ti(O ⁱ Pr) ₃ (thd)] ₂ [41]	Ti(O ⁱ Pr) ₂ (tbaoc) ₂ [42, 43]	Ti(O ⁱ Pr) ₂ (acac) ₂ [44]
Terminal	1.766	1.784	1.8017	1.784	1.804
Terminal	1.799	1.782	1.8160	1.784	1.788
Terminal	1.804				
Bridging	1.893	1.969	1.9677		
Bridging	2.066	2.101	2.0941		

Table 5 Partial charge on zirconium and titanium atoms. Calculated for unmodified and for Hacac, Hthd, H₂dea and tbaoc modified compounds

Compound	δ Zr	Compound	δ Ti
Zr ₄ (O ⁿ Pr) ₁₆ [33]	0.639	Ti(O ⁱ Pr) ₄ [40]	0.614
[Zr(O ⁱ Pr) ₄ (HO ⁱ Pr)] ₂ [30]	0.641	[Ti(O ⁱ Pr) ₃ (acac)] ₂ [41]	0.632
[Zr(O ⁱ Pr) ₃ (acac)] ₂ [35]	0.658	Ti(O ⁱ Pr) ₂ (acac) ₂ [41]	0.638
Zr(O ⁱ Pr)(acac) ₃ [35]	0.691	[Ti(O ⁱ Pr) ₃ (thd)] ₂ [41]	0.618
[Zr(O ⁱ Pr) ₃ (thd)] ₂ [36, 38]	0.644	Ti(O ⁱ Pr) ₂ (thd) ₂ [44]	0.620
Zr(O ⁱ Pr)(thd) ₃ [36]	0.648	Ti(O ⁱ Pr) ₂ (tbaoc) ₂ [42, 43]	0.621
[Zr ₂ (O ⁿ Pr) ₆ (OC ₂ H ₄) ₂ NH] ₂ [37]	0.658		
Zr(dea) ₃ (Zr(O ⁱ Pr) ₃) ₂ (ⁱ PrOH) ₂ [37]	0.657		
[Zr(O ⁱ Pr) ₃ (tbaoc)] ₂ [39]	0.661		
Zr(O ⁱ Pr) ₂ (tbaoc) ₂ [39]	0.675		

from literature [39, 40] on zirconium alkoxide precursors, introduction of 1 mol equivalent of acetylacetonate (Hacac) to zirconium isopropoxide leads to a pronounced elongation of all zirconium-oxygen bonds in the modified complexes (see Table 3). This effect is noticeable but less pronounced, when the modification is performed with an analogous ratio of more bulky 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd). Packing effects can play a certain role in this latter case. The modification with 1 mol equivalent of the *a*-symmetric *tert*-butylacetoacetate results in a complex that has a strong variation in bond lengths [40, 41], with some of them being strongly elongated compared to the bond lengths in the unmodified precursor. The terminal alkoxide ligands in $Zr\{\eta^3\mu_2\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Zr}(\text{O}^i\text{Pr})_3]_2(\text{}^i\text{PrOH})_2$, obtained upon the modification of zirconium isopropoxide with 1 mol equivalent of H₂dea [38], seem to form an exception; the bond lengths are slightly shortened.

For titanium precursors, a comparison of bond lengths in modified and unmodified compounds is shown in Table 4. The only structure of an unmodified precursor, Ti(OⁱPr)₄, has recently been reported by Schubert [41]. It should be noted that the unmodified precursor is penta-coordinated while the Hthd, Hacac [42] and tbaoc [43, 44] modified structures are hexa-coordinated. The metal-oxygen bond lengths of the alkoxide ligands in these modified compounds are again noticeably elongated compared to those in the unmodified precursor.

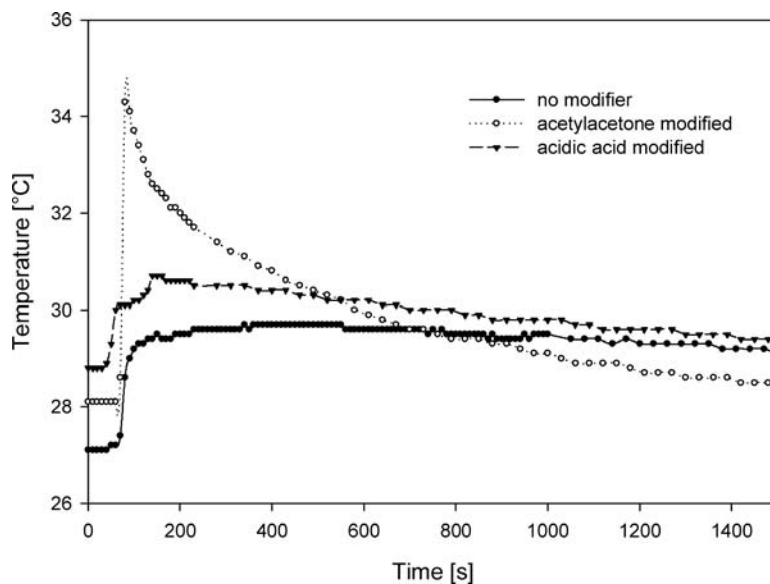
The evident trend to elongation of metal-oxygen bonds indicates thus that introduction of modifying ligands is increasing the charge distribution in the complexes. Partial charge distribution calculations performed according to the

model proposed by Henry et al. [27] give a semi-quantitative estimation of this effect (see Table 5). The increase of the effective positive charge at the metal atoms compared to unmodified precursors is beyond any doubt.

Chelating ligands are noticeably accelerating hydrolysis-polycondensation

Simple calorimetric measurements were performed to evaluate the temperature effect of the introduction of the modifying ligands and water addition to modified and unmodified precursor solutions. Zirconium *n*-propoxide was modified with 1 mol equivalent of Hacac, diethanolamine, triethanolamine or acetic acid. Subsequently, 2 mol equivalents of water were added and the observed heat effects are depicted in Fig. 4. A precipitate immediately formed upon addition of the water/propanol mixture to the unmodified and acetic acid modified precursors. A clear yellowish sol formed from the solution containing the Hacac modified precursor; however, a small amount of crystals were formed about one hour after the addition of the water. These crystals were identified as Zr(acac)₄, present in the solution before hydrolysis takes place [36]. For both the acetic acid modified and unmodified precursor an increase in temperature is observed upon the addition of water, followed by a modest heat release due to the hydrolysis and condensation sequence. The temperature remains unchanged after the initial increase and subsequent decrease at a rate, which is lower than the expected exponential decrease in temperature due to equilibration with the surroundings. In contrast, the addition of water to precursors modified with

Fig. 4 Temperature variation on addition of water to the unmodified and modified zirconium propoxides



Hacac, diethanolamine and triethanolamine (the latter not shown in Fig. 4) leads to an instant temperature increase. This noticeably quicker temperature increase suggests that the reactivity of the precursor molecule has increased upon modification and that hydrolysis occurs almost instantaneously.

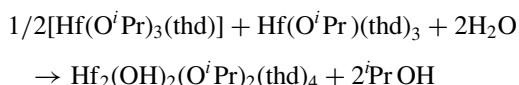
In an earlier calorimetric study on the hydrolysis and condensation reactions of titanium alkoxides by Blanchard et al. [46], the exothermic behavior of the hydrolysis and condensation sequence was attributed to an increase in the coordination number. The authors assumed that the hydrolysis, oxolation and alkoxolation are substitution reactions and do not involve coordination expansion. The increase of the coordination number was proposed to take place in the early stages of hydrolysis, i.e., the authors assumed that the hydrolysis proceeds according to a nucleophilic addition reaction (S_N2 mechanism), which in fact is not true for metal alkoxides [23]. It is necessary to underline that the increase in a coordination number itself is in literature **not** associated with exothermal effects if not leading to increased charge distribution [47]. The structural data on titanium precursors indicate that no changes in coordination number occur during the hydrolysis—it remains equal to 6 from the modified precursor to the final oxide material, which may be one of the explanations to why the heat effect is lower for the modified species. Qualitatively observed increase in the heat effect from acetylacetone modified zirconium alkoxide is indicating a possibility of better densification, both higher charge distribution and higher coordination numbers achieved through hydrolysis-polycondensation in this case. This is not unexpected as the coordination number of zirconium atoms increases finally from 6 to 7–8 in this process.

The obtained data show unequivocally that the reactivity towards water is definitely not decreased on application of the chelating ligands.

Chelating ligands are highly mobile and do not hinder condensation

One of the most evident illusions that dominated the ideas about the reactions of modified alkoxide precursors in the 1980-es was that they remain attached to the same metal atom they originally belonged to. It was common to consider the chelating effect to result in high activation energy of ligand transfer. The experimental arguments against this idea have been first provided in the brilliant work of Wengrovius in 1986 [48], where the transfer of β -diketonate ligands between modified aluminium alkoxide molecules has been thoroughly investigated by NMR. The studies were done in hydrocarbon solvents and showed that the equilibria there could be achieved in the time span from minutes to hours. The facile mobility of carboxylate ligands has also recently been proven by U. Schubert et al. in the NMR studies of zirconium oxo-carboxylate complexes [49]. We could observe the same time scale in hydrocarbon solvents for the β -diketonate modified zirconium alkoxides [36, 37]. Much more important, we could see that the ligand transfer process was very strongly accelerated by polar solvents such as alcohols. On hydrolysis it became practically immediate for zirconium and hafnium complexes. We observed, for example, an immediate precipitation of hydroxy-di-substituted hafnium propoxide, $Hf_2(OH)_2(O^iPr)_2(thd)_4$,—a product of both hydrolysis and hydroxylation (condensation) on addition of water to a mixture of mono- and tri-substituted

complexes [37]:



It should be noted that in the absence of hydrolysis no di-substituted compounds are formed on modification of zirconium or hafnium propoxides by β -diketones—only mono- and tri-substituted intermediates can be observed in both solid state and solution [36, 37]. The facile mobility of ligands on hydrolysis and their inability to hinder condensation reactions is a well structurally confirmed fact.

True effect of the chemical modification

We could clearly see from the arguments listed above that the chemical modification does not lead to decreased rate of hydrolysis and polycondensation reactions, however, it does really result in slowing down or even preventing the gelation and, especially, the uncontrolled precipitation on addition of water. The answer to this question cannot be found in that addition of chelating ligands or protons (an acid) “inhibits” polycondensation as it was supposed in [50]. In particular, protons have been proved to be catalysts of the polycondensation reaction and the addition of acids permitted this reaction to occur quicker than hydrolysis for silicon alkoxides and provide well-identified polymer chain structures [13, 51]. Catalytic effect cannot transform into inhibition. There is fundamental difference between the two phenomena: the catalyst facilitates formation of the intermediate activated state, in the present case the cationic species in the S_N1 mechanism, while the inhibitor changes the reaction pathway, hindering the original products to be formed. In the case of sol-gel process, we could see that the chemical modification was having catalytic effect on the homogeneous reactions of hydrolysis-polycondensation. Its role then is in offering a different reaction pathway than the polymerization reaction itself, which can only be a heterogeneous process as we have already deduced earlier [52]. The heterogeneous systems, dispersions, are simply stabilized through the interaction of the ligands, collected on the surface of the particles, with the solvents. The dispersion particles have a dense core and a shell responsible for their stabilization, i.e. they have a structure typical of micelles. We propose to call these specific constructions Micelles Templated by Self-Assembly of Ligands (MTSALs) because of the special role, played by ligands in their surface stabilization. In fact the formation of such constructions has been hinted earlier by Harris [20] and by Bartlett [53].

Application of the MTSAL mechanism for preparation of new materials

It should honestly be mentioned that in many applications the true mechanism of the sol-gel process does not play a decisive role. The synthesis of zirconia nanoparticles from, for example, the solutions, modified by acetylacetone [54], is in its logics quite analogous to the Stoeber process (see [21,55]). Whether kinetic factors play any role, as for spherical particles of silica in the Stoeber process or are of no importance as for zirconia synthesis in the polar solvents from direct MTSALs, the resulting objects have essentially the same appearance. These are spherical dense particles. The addition of strong acids to the water solution used for hydrolysis delays or prevents gelation independently, whether it causes stabilization of direct micelles or “inhibits polycondensation”. We sought thus examples that would provide an unequivocal demonstration of the phenomenon of micellar self-assembly. One such possibility, demonstrated below, deals with the formation of inverted micelles in a water-in-hydrocarbon emulsion and further transformation of these micelles on contact with a solid surface. The other possibility is a new approach to microporous transition metal oxide membranes, using a chelating-and-bridging ligand.

Hollow spheres—host for encapsulation of hydrophilic matter

Metal alkoxides have not been applied earlier for creation of shells for encapsulation. Encapsulation by shells created from silicon alkoxides [19, 56] was considered only as a possibility to host hydrophobic matter, dissolved in hydrocarbon solvent or oil. Possibility to apply the inverted micelles for encapsulation without surfactants has never been considered. In fact, if the products of hydrolysis-polycondensation were polymeric molecules with fractal structure, they would not be able to prevent efficiently the diffusion of water through the layer on the surface of emulsion drops. Unhindered water diffusion had to result finally in precipitation in the whole volume of the precursor solution in a hydrocarbon solvent. Having observed earlier the formation of dense films from the alkoxide precursors modified by β -diketones [57], we were convinced that the hydrolysis of modified alkoxides results generally in micellar self-assembly and then not fractal, but dense structures. We wanted also to apply a sensitive marker for proving even the opposite, i.e. that the hydrocarbon solvent does not diffuse efficiently inside the inverted micelles. For the role of this marker we have chosen red blood cells, erythrocytes. The solution containing erythrocytes was prepared by diluting 0.2 ml of fresh blood (donated by the corresponding author) with

Fig. 5 Zirconia spheres with encapsulated erythrocyte solution

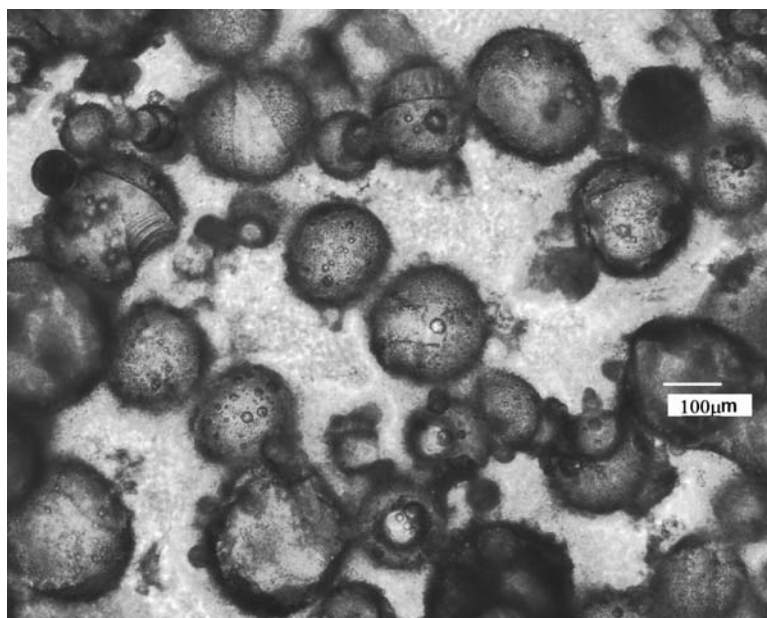
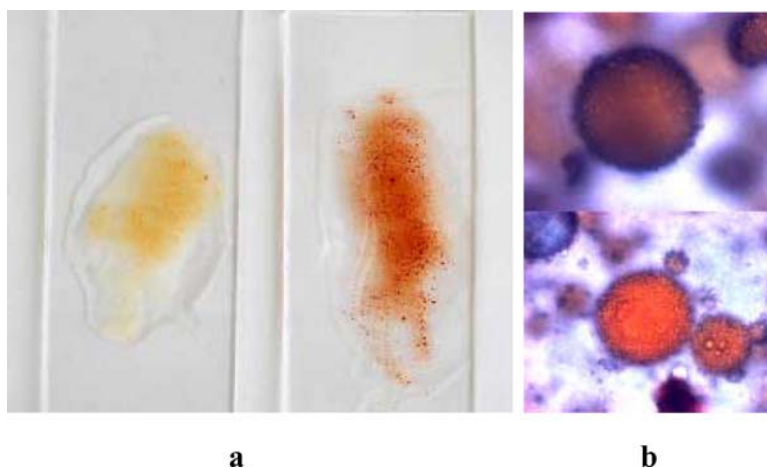


Fig. 6 Emulsions of iron thiocyanate (0.05 M water solution with respect to both $\text{Fe}(\text{NO}_3)_3$ and KSCN): (a) in reflected light (supported by zirconia shells to the left, unsupported—to the right) and (b) in transient light (supported—upper picture, unsupported—lower picture)



20 ml of isotonic NaCl solution. 0.5 ml of this bright red solution, containing undestroyed erythrocytes according to microscopic observation, were added by syringe on vigorous shaking to the of solution of $\text{Zr}(\text{O}^n\text{Pr})_3(\text{thd})$ (isolated according to [37]) in 5 ml dry hexane (for details see Experimental). The water phase was immediately transformed into tiny light brick-red spheres hardly distinguishable by a bare eye. The solution above them remained completely clear for at least one hour, when light opalescence started to appear. Investigation of the spheres, immersed into paraffin oil, under optical microscope (see Fig. 5) showed major part of them to have size of 100–200 μm (0.1–0.2 mm). No free water phase could be observed.

The spheres were stable on shaking in the hexane solution but were destroyed by putting a cover glass over them. The immediate observation of the water phase released then into paraffin oil (about 3 h after encapsulation)

showed a fraction of undestroyed erythrocytes (which are highly sensitive and destroyed rather quickly on contact with hexane).

The size of the spheres is determined in the first hand by that of the droplets in the originally formed emulsion. The emulsions obtained by mechanical stirring have actually rather varied size of the droplets—the majority are 100–200 μm as stated above, but they are surrounded by much smaller ones attracted to their surface by the colloid forces. It should be mentioned that the droplets coated by the shells, produced from modified alkoxide, have the same appearance as the droplets of the mechanically produced emulsion (see Fig. 6). The difference can be seen in their color and the stability in time: the droplets of mechanical emulsion coalesced, producing big droplets of water solutions, while the zirconia shells remained unchanged in hexane for at least a week. Dispersion of the added water solution with the help

Fig. 7 Luminescent microspheres localized within the shells formed on the interface of a water suspension in hexane solution of thd-modified zirconium propoxide

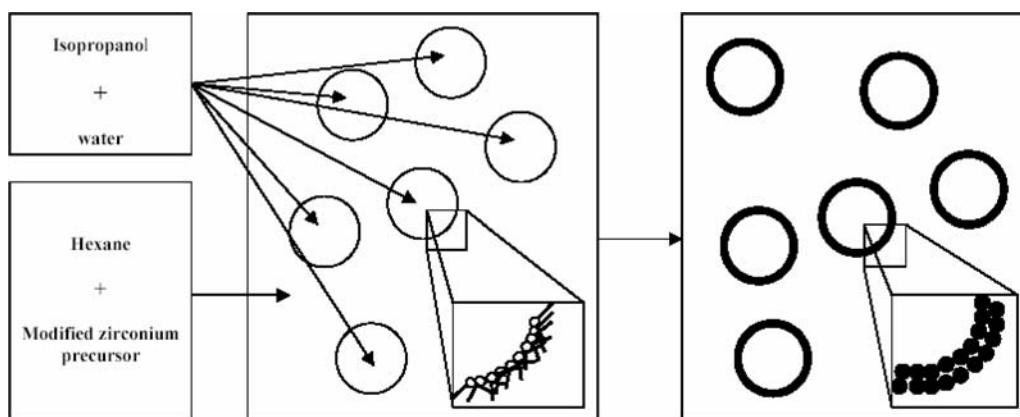
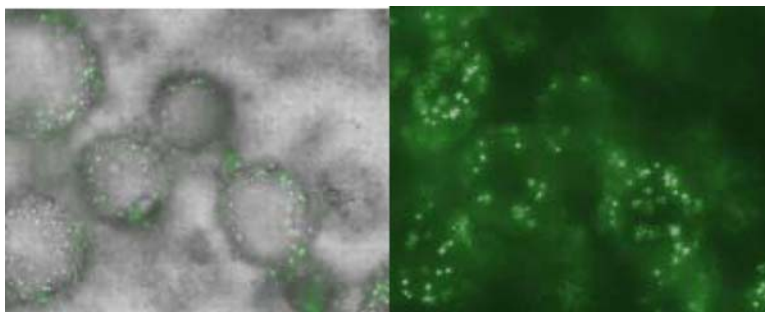


Fig. 8 The strategy for creation of *nano*-spheres using the MTSAL concept

of an ultrasound bath gave, quite logically, smaller spheres, about $20\ \mu\text{m}$ in diameter. It should be mentioned that the color of the obtained spheres is generally lighter in reflected and darker in the transient light than that of the encapsulated solution and the smaller the size of the spheres is, the lighter is the color obtained on reflection (see Fig. 6). This shows that, in agreement with the laws of fundamental optics, the reflection from the surface of the spheres starts to dominate over adsorption by the encapsulated solution, when the size of the spheres approaches the wavelength of the visual light (the photons that enter the spheres are quenched by complete inner reflection and interference).

In order to show that the formation of the shells occurs through self-assembly mechanism, directed by the amphiphilic nature of the hydrated oxide containing residual (hydrophobic) modifying ligands, we have applied the same procedure for encapsulation of a water suspension of green fluorescing $2.2\ \mu\text{m}$ polystyrene microspheres (Duke Scientific Corp., Palo Alto, CA, USA). These suspensions are commonly used in the microbiological studies and are fairly stable in water. Polystyrene, however, is a weakly hydrophobic material, which meant it should have been extracted into the amphiphilic shell in the process of encapsulation. The microscopic observations (see Fig. 7) were completely in accordance with our expectations—the microspheres have not escaped from the droplets into hexane solution as the formation of the shells is a quick process, but

turned to be located inside the shells and not in the volume of the droplets.

It appeared challenging to achieve further decrease in the size of the spheres, which required an emulsion with smaller size of the water droplets. As the modifying ligands in combination with the hydrolyzed alkoxide species are amphiphilic and act as a surfactant, it was necessary to add a co-surfactant to decrease the size of the droplets. We introduced thus water in the form of solution in the parent alcohol (see Fig. 8).

Addition of water solutions in parent alcohol (HS1–HS9) resulted in clear colloids, not separating in time, in contrast to the cases, where only water was used as the second solvent. The investigation of the obtained objects by Transmission Electron Microscopy (TEM) revealed as expected much smaller spheres. The average diameter of the spheres (typically about 200–250 nm, Fig. 9) and statistical variation within a sample vary to some extent, being dependent of water : alcohol : hydrocarbon ratios.

Common feature of the obtained spheres is very small thickness of the walls, below 10 nm, as it can be deduced from the Fig. 9. Drying of the samples leads to opening of majority of the spheres. This makes this family of spheres interesting for different kinds of delivery applications, as it should be possible to open them in a controlled way. In the view of their smaller size, the encapsulation experiments have been carried out with water/alcohol solutions of small molecules, in particular, dyes such as Eriochrome Black T (Erio-T, an

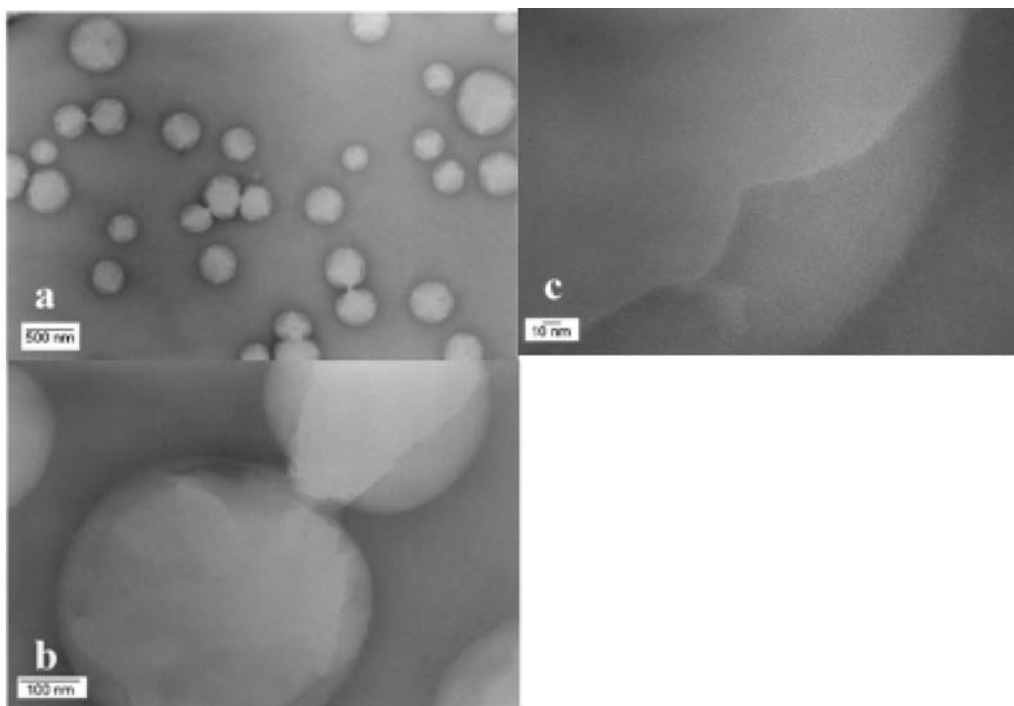
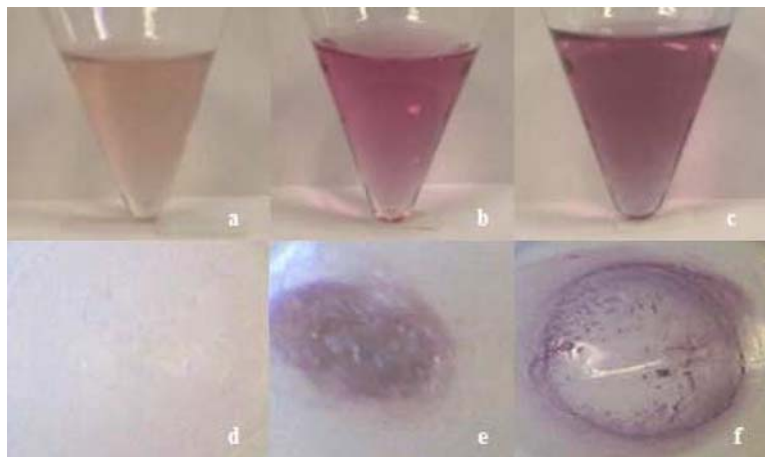


Fig. 9 TEM images of the hollow metal oxide nanospheres: (a) an overview, (b) coalescing spheres with connected hollow rooms, (c) a crack in a sphere (Sample HS1)

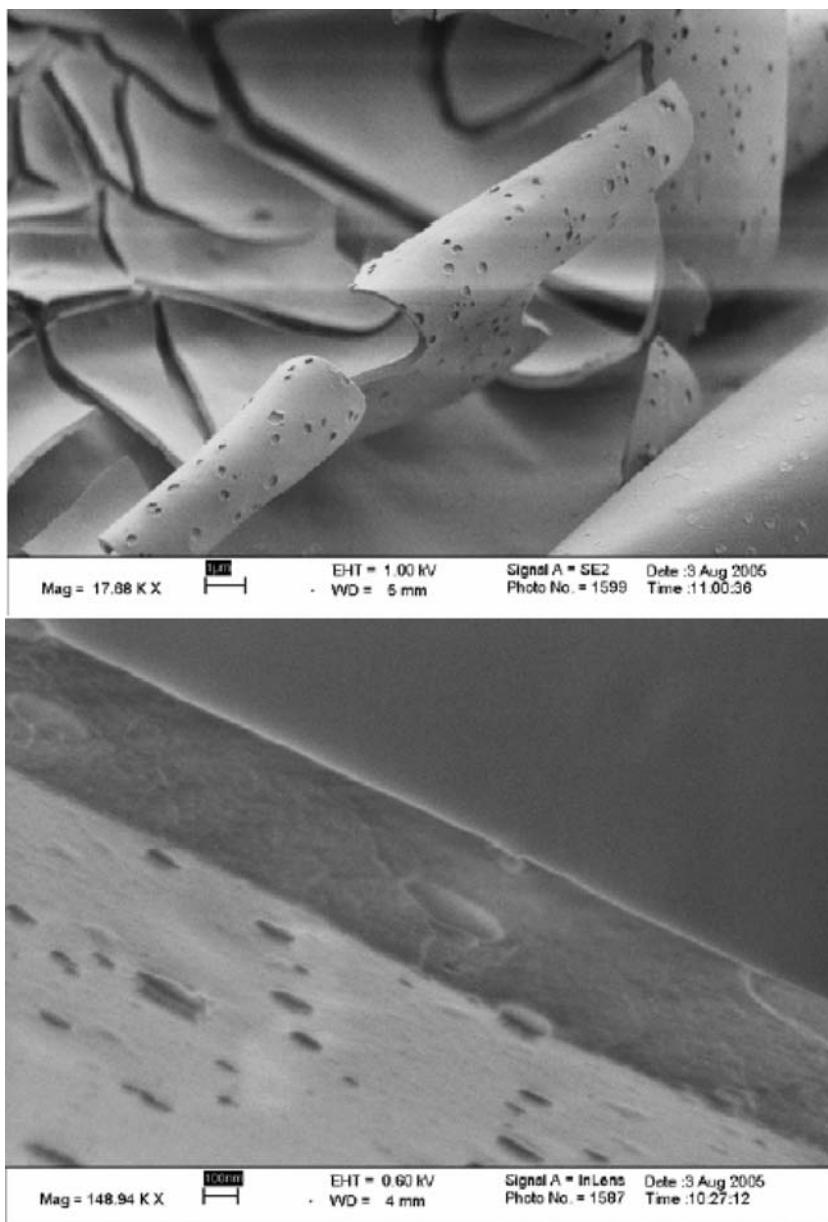
Fig. 10 Eriochrom Black T solutions with the same total concentration in (a) emulsion formed by introduction of propanol/water solution of the dye into hexane solution of the modified precursor, (b) emulsion formed by introduction of propanol/water solution of the dye into propanol solution of the modified precursor, (c) solution in hexane/propanol/water mixture as in (a) but in the absence of precursor. The powder obtained upon drying of solution (a)–(c) is depicted in (d)–(e), respectively



ionic organic salt with intensive purple color). The strongly colored solutions were used as hydrolysis medium. The dye-containing propanol/water solutions were added to solutions of Hacac modified zirconium propoxide precursors in, either, hexane or isopropanol for comparison. The expected size of the spheres (200–250 nm) was in this case smaller than the wavelength of the visible light, which meant that in case of encapsulation the colour had practically to disappear, while hydrolysis without encapsulation could not lead to considerable colour changes. The observed colours of obtained solutions were in complete agreement with expectations (see Fig. 10)

The study of Erio-T encapsulation in acac-modified zirconium precursors provided an additional unexpected confirmation for selective positioning of the modifying ligands on the surface of the shells. After about 30 min after the addition of the water/propanol solution of Erio-T to a hexane solution of the modified zirconium precursor, we could observe precipitation of well-shaped crystals of $Zr(acac)_4$ with practically quantitative yield(!) The interaction with an ionic organic salt was supposedly providing the shells with a surface charge, which stabilized them and at the same time caused the increased mobility and finally release of the heteroligands.

Fig. 11 Films prepared on carbon grids from the colloids containing hollow spheres



It appeared extremely interesting to evaluate the stability of these latter thin-walled shells in the presence of humidity and shear forces. This was made by drying a colloid solution, containing “hollow” (water solution filled) spheres on carbon grids, followed by investigation by Scanning Electron Microscopy (SEM). This treatment (see Fig. 11) resulted in formation of dense films incorporating spherical cavities.

This deep transformation of the original spherical shells indicates that the mobility of ligands is actually very high even after the formation of the capsules. Films with random distribution of closed spherical cavities that can be filled with a hydrophilic component are a new and interesting type of material.

Microporous materials

The observed trend to localization of ligands on the surface of sol particles and their continuous mobility provided also explanation for the difficulties in obtaining non-silica oxide materials with reproducible microporosity. Application of chelating only ligands commonly results in dense films [57]. The latter can be provided with cavities or macropores, but are of no interest for the application, where microporosity is required, e.g. for the preparation of oxide membranes. Microporosity can be achieved only through the retention of ligands inside the volume of micelles and thus requires immobilization of ligands. We have proposed

to apply the ligands, possessing both chelating and bridging properties, e.g. diethanolamine ones, for this purpose. In our study of modification of the zirconium propoxides by diethanolamine we observed initially the formation of four-member chain complexes of the $[\text{Zr}_2(\text{OR})_6(\text{OC}_2\text{H}_4)_2\text{NCH}_3]_2$ type analogous to the *n*-propoxide complex with methyl-diethanolamine described earlier by Gainsford et al. [58]. These complexes turned to be highly unstable in solution and even in the solid phase, rapidly transforming into $\text{Zr}\{\eta^3, \mu_2\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Zr}(\text{OR})_3]_2$ molecules [38]. The latter had a principally different structure with a highly coordinated (nonacoordinated) central core and hexacoordinated terminal sites. The high and very symmetric coordination with the ligands all connected in the same chelating-and-bridging mode was indicating that the mobility of these ligands on hydrolysis was decreased. Its structure revealed also an approach to related heterometallic precursors, involving one bigger tetravalent atom, such as zirconium or hafnium and a smaller one, for example, titanium. Such heterometallic precursors, $\text{Zr}\{\eta^3, \mu_2\text{-NH}(\text{C}_2\text{H}_4\text{O})_2\}_3[\text{Ti}(\text{OR})_3]_2$, $\text{R} = {}^i\text{Pr}$ and ${}^n\text{Pr}$ [38] were formed with quantitative yields on mixing zirconium and titanium propoxides in molar ratio $\text{Zr} : \text{Ti} = 1 : 2$ and adding 3 equivalents of H_2de . These compounds turned to be extremely attractive as precursors in several ways. Their hydrolysis and thermal treatment under rather mild conditions (800°C in 30 min) gave a single-phase srilankite, ZrTi_2O_6 , material [59]. Srilankite has earlier been known as a volcanic mineral and was prepared by synthesis under high pressure (20 kbar and higher) and high temperatures [60]. It was found to be highly chemically inert and to possess very attractive dielectric properties. The films obtained by dip-coating from prehydrolysed solutions of the abovementioned bimetallic complexes with subsequent thermal treatment at 400°C in 3 h (conditions corresponding to the removal of diethanolamine ligands) were really shown to be useful as hydrothermally stable microporous membranes. They displayed high permeance for small molecules, such as O_2 , N_2 or H_2O , but stopped almost completely already such molecules as butane, C_4H_{10} [59]. What appears important to mention in connection with the mechanism of sol-gel processing for this case, is that porosity of both powders and films, prepared from these precursors, was strongly dependent on the acidity of the water solution used for prehydrolysis. The higher the amount of acid added the lower was final porosity (and higher the pH in the obtained solution). The acid reacted thus not as a catalyst but led to protonation of the basic ligands and facilitated their mobility and removal.

Conclusions

The sol-gel chemistry for metal alkoxides is clearly different from what it has been earlier assumed. These compounds are

rather strong Lewis bases and very weak Lewis acids and the ligand exchange and hydrolysis proceeds for them through a proton-assisted $\text{S}_{\text{N}}1$ mechanism analogous to that for acid-catalyzed hydrolysis of silicon alkoxides, and not an $\text{S}_{\text{N}}2$ mechanism, proved for the base-catalyzed hydrolysis of silicon alkoxides. The reactivity of metal alkoxide precursors is increased rather than decreased upon addition of modifying ligands just as it also happens with silicon alkoxides. The high reactivity of the modified precursors causes the ligand exchange, hydrolysis and also the condensation reactions to proceed for metal alkoxides almost instantaneously upon the addition of water. Another striking difference with traditional silica sol-gel is the large mobility of the modifying ligands. The whole process of sol formation is thus directed not by kinetics of hydrolysis and polycondensation, but by the self-assembly of ligands. The modifying ligands are forming the particles of sols through their interaction with the solvents and can stabilize dispersions in essentially the same way as surfactants. The formed hydrated oxides are hydrophilic, which means that the polar solvents are favoring the direct and non-polar ones—inverted micellar self-assembly. Application of ligands displaying both chelating and bridging binding modes results in decreased ligand mobility and opens approaches to powders and coatings with controlled microporosity.

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