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Oxide Gels and Ceramics Prepared by a Nonhydrolytic Sol–Gel Process

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Anhydrous gels have been prepared by a nonhydrolytic sol–gel process using a direct condensation reaction between metal carboxylates $\mathrm{M(O_2CR)}_x$ and metal alkoxides $\mathrm{M'(OR')}_y$ in nonpolar, aprotic solvents such as toluene or paraffin. This general procedure has been optimized for anhydrous zirconia gels prepared by reaction of zirconium tetraacetate with zirconium tetra-*n*-propoxide in toluene and for anhydrous zircon gels from silicon tetraacetate and zirconium tetra-*n*-propoxide in toluene. The properties of the anhydrous gels were examined by FTIR, DTA, TGA, MS, and ^{29}Si MAS NMR. The analyses show that a condensation reaction between the acetate and the alkoxide takes place, yielding a M′–O–M network and carboxylic acid ester as a coproduct. The extent of the condensation has been determined to be 71% in the case of the anhydrous zircon gels and 60% in the case of the anhydrous zirconia gels. Remaining traces of the solvent and ester are easily and completely removable at moderate temperatures. The crystallization of the anhydrous gels has been studied by X-ray powder diffractometry.

Introduction

We have examined a nonhydrolytic sol–gel process to obtain anhydrous gels and ceramics by a direct condensation of appropriate metal–organic compounds such as alkoxides and carboxylates according to

$$m\mathrm{M(OR)}_n + n\mathrm{M'(O_2CR')}_m \rightarrow \mathrm{M}_m\mathrm{M'}_n\mathrm{O}_{nm} + nm\mathrm{ROCOR'} \quad (1)$$

This procedure is related to the condensation reaction (transesterification) of trialkylsilyl acetates (silyl esters) $\mathrm{R'_3Si(OAc)}$ with metal alkoxides $\mathrm{M(OR)}_x$ (eq 2) described by Bradley and Thomas.[1,2] Trialkylsiloxides $\mathrm{M(OSiR'_3)}_x$ of titanium, zirconium, and other metals were obtained by this method.

$$\mathrm{M(OR)}_x + x\mathrm{R'_3Si(OR'')} \rightarrow \mathrm{M(OSiR'_3)}_x + x\mathrm{R''CO_2R} \quad (2)$$

Recently, Iwasaki et al.[3] have mentioned the condensation of silicon tetraacetate $\mathrm{Si(OAc)_4}$ with titanium(IV)acetylacetonatotriisopropoxide ($\mathrm{Ti(AcAc)(OiPr)_3}$) in THF.

In addition, a number of papers dealing with a similar nonhydrolytic sol–gel process for the preparation of oxide gels and ceramics utilizing the direct condensation of metal halides with metal alkoxides releasing alkyl halides as coproduct (eq 3) were published by Corriu et al.[4–6] and Acosta et al.[7,8]

$$m\mathrm{MX}_n + n\mathrm{M'(OR')}_m \rightarrow \mathrm{M}_m\mathrm{M'}_n\mathrm{O}_{nm} + nm\mathrm{R'X} \quad (3)$$

This approach is based on a procedure of preparing nonmetal oxides published by Gerrard et al.[9] The anhydrous gels obtained by our nonhydrolytic method contain neither halides, hydroxo groups, nor traces of alkyl halides, which would affect the purity of oxide ceramics originating from them negatively.

The conventional sol–gel process runs via hydrolysis of metal–organic starting compounds such as alkoxides $\mathrm{M(OR)}_n$, halides MX_n, oxohalides $\mathrm{MO}_a\mathrm{X}_{(n-2a)}$ and carboxylates $\mathrm{M(O_2CR)}_n$ in polar, protic, and nucleophilic solvents such as alcohols (eqs 4 and 5).[10–12]

$$\mathrm{MQ}_n + x\mathrm{H_2O} \leftrightarrow \mathrm{MQ}_{n-x}\mathrm{(OH)}_x + x\mathrm{HQ} \quad (4)$$

$$\mathrm{M'Q'}_m + y\mathrm{H_2O} \leftrightarrow \mathrm{M'Q'}_{m-y}\mathrm{(OH)}_y + y\mathrm{HQ'} \quad (5)$$

The step of hydrolysis is succeeded immediately by a reversible (hetero-) condensation reaction by which the desired M′–O–M bridges are formed (eq 6).

In bicomponent (multicomponent) gels undesired homocondensation generating M–O–M links (eq 7) may occur.

$$\mathrm{MQ}_{n-x}\mathrm{(OH)}_x + \mathrm{M'Q'}_{m-y}\mathrm{(OH)}_y \leftrightarrow \mathrm{Q}_{n-x}\mathrm{(OH)}_{x-1}[\mathrm{M{-}O{-}M'}]\mathrm{Q'}_{m-y}\mathrm{(OH)}_{y-1} + \mathrm{H_2O} \quad (6)$$

$$\mathrm{MQ}_{n-x}\mathrm{(OH)}_x + \mathrm{MQ}_{n-x}\mathrm{(OH)}_x \leftrightarrow \mathrm{Q}_{n-x}\mathrm{(OH)}_{x-1}[\mathrm{M{-}O{-}M}]\mathrm{Q}_{n-x}\mathrm{(OH)}_{x-1} + \mathrm{H_2O} \quad (7)$$

The hydrolysis and the promptly succeeding condensation reaction are generally hard to control, especially

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if multicomponent gels are to be prepared by using metal–organic compounds with quite different reaction rates for the hydrolysis. The most severe complication is homocondensation by which formation of inhomogeneities is promoted. To avoid too rapid hydrolysis and to allow for a slow gelation process, several approaches have been suggested. Widely used is the prehydrolysis of the less reactive precursor[13,14] before adding the more reactive one or the use of heterometallic compounds with preformed M′–O–M bridges. However, in the latter case the M′–O–M bridge may be cleaved during hydrolysis and thus homocondensation becomes possible again. Alternatively, retarded hydrolysis can be achieved by adding water to the reaction mixture in situ.

Such homogeneous water supplying reactions like esterification (eq 8) or the formation of acetals (eq 9) provide a low but steady concentration of water.

$$\mathrm{ROH} + \mathrm{R'COOH} \leftrightarrow \mathrm{ROCOR'} + \mathrm{H_2O} \qquad (8)$$

$$\mathrm{RCHO} + 2\mathrm{R'OH} \leftrightarrow \mathrm{RCH(OR')_2} + \mathrm{H_2O} \qquad (9)$$

The benefits of such controlled hydrolyses may be offset by an increased amount of organic waste included within the gels. Another general drawback of the hydrolytic route is the reversibility of the condensation reaction which may induce phase separation during gelation.

The complete removal of water and/or polar solvents from hydrolytic gels usually requires drastic conditions because of their relatively strong polar interactions with the gel network. Especially unreacted hydroxo groups and surplus water resist tough drying conditions, and this may result in destructive shrinking of initially monolithic gels. Thus, development of alternative preparative routes avoiding at least some of the drawbacks mentioned before seems to be worthwhile.

General Remarks

To overcome some complications of hydrolytic sol–gel processes, we have explored an alternative nonhydrolytic approach to (multicomponent) oxide gels and ceramics. In this paper we describe the preparation of anhydrous gels of zirconia ZrO_2 and zircon $ZrSiO_4$ by using a direct condensation reaction of metal alkoxides $M(OR)_x$ with metal carboxylates $M'(O_2CR')_y$ releasing a carboxylic acid ester as coproduct (eq 10). The aim is to avoid homocondensation in principle so that in the case of bicomponent (multicomponent) anhydrous gels the network should contain the metals M and M′ in a perfectly alternated sequence.

$$\mathrm{M(OR)}_x + \mathrm{M'(O_2CR')}_y \rightarrow \\ \mathrm{(RO)}_{x-1}[\mathrm{M{-}O{-}M}](\mathrm{O_2CR'})_{y-1} + \mathrm{ROCOR'}$$

$$\mathrm{M = Zr;\ M' = Si, Zr;\ R = C_3H_7;\ R' = CH_3} \qquad (10)$$

The virtually nonexisting nucleophilic character of the ester formed as coproduct drastically reduces the reverse reaction of cleaving the M′–O–M bridges. Reaction 10 is carried out in a nonpolar, aprotic, nonnucleophilic solvent such as aromatic or aliphatic hydrocarbons.

In our experiments we employed toluene. This type of solvent and the ester coproduct are easier to remove from the gels because of their weaker interactions with the gel network compared to more polar solvents. The complete process can be formulated as follows:

$$y\mathrm{M(OR)}_x + x\mathrm{M'(O_2CR')}_y \rightarrow \\ \mathrm{M}_y\mathrm{M'}_x\mathrm{O}_z(\mathrm{OR})_{xy-z}(\mathrm{O_2CR'})_{xy-z} + z\mathrm{ROCOR'} \qquad (11)$$

The stochiometric parameter z is directly equivalent to the reaction progress and ranges from zero at the very beginning to its maximum value of xy when full condensation is achieved.

Experimental Section

The starting materials for the zirconia gels (eq 12) were zirconium tetraacetate $Zr(OAc)_4$ and zirconium tetra-*n*-propoxide $Zr(OPr^n)_4$ and in the case of the zircon gels (eq 13)

$$\mathrm{Zr(OPr^{\mathit{n}})_4} + \mathrm{Zr(OAc)_4} \rightarrow \\ \mathrm{Zr_2O}_z(\mathrm{OAc})_{4-z}(\mathrm{OPr^{\mathit{n}}})_{4-z} + z\mathrm{AcOPr^{\mathit{n}}} \qquad (12)$$

$$\mathrm{Zr(OPr^{\mathit{n}})_4} + \mathrm{Si(OAc)_4} \rightarrow \\ \mathrm{ZrSiO}_z(\mathrm{OAc})_{4-z}(\mathrm{OPr^{\mathit{n}}})_{4-z} + z\mathrm{AcOPr^{\mathit{n}}} \qquad (13)$$

zirconium tetra-*n*-propoxide $Zr(OPr^n)_4$ and silicon tetraacetate $Si(OAc)_4$. The $Zr(OPr^n)_4$ used was commercially available as a 70% solution in *n*-propanol (Fluka) which was treated for 24 h in vacuo to remove all *n*-propanol,[16] yielding a waxlike solid, highly soluble in toluene.

The absence of *n*-propanol and hydroxo functions in general was proven by FTIR spectra, which did not show any absorption bands caused by OH valence vibrations at about 3500 cm^{-1}. *n*-Propanol must be absent in order to prevent the undesired formation of water by a competitive reaction with the acetate (eqs 14 and 15). The acetates were prepared by procedures described by Schuyten[17] ($Si(OAc)_4$) and Ludwig[18] ($Zr(OAc)_4$).

$$\mathrm{M(OAc)}_x + z\mathrm{HOR} \rightarrow \mathrm{M(OAc)}_{x-z}(\mathrm{OH})_z + z\mathrm{AcOR} \qquad (14)$$

$$2\mathrm{M(OAc)}_{x-4}(\mathrm{OH})_z \rightarrow \\ (\mathrm{AcO})_{x-z}(\mathrm{OH})_{z-1}[\mathrm{M{-}O{-}M}](\mathrm{OAc})_{x-z}(\mathrm{OH})_{z-1} + \\ \mathrm{H_2O} \qquad (15)$$

In both cases 0.01 mol of the acetate compounds was partially dissolved in 60 mL of dry toluene and heated to boiling temperature. A solution of 0.01 mol of *n*-propanol-free zirconium tetra-*n*-propoxide in 40 mL of dry toluene was added dropwise to the boiling acetate solutions. While refluxing the reaction mixtures for 3 days, they became increasingly opaque. The liquid phases were removed from the anhydrous gels by vacuum distillation at temperatures raised to 150 °C. All procedures were carried out under a dry argon atmosphere to exclude moisture.

CAS-Registry numbers and chemical hazards: $Si(OAc)_4$: [562-90-3], corrosive, moisture-sensitive. $Zr(OAc)_4$: [7585-20-8], corrosive, moisture sensitive. $Zr(OPr^n)_4{\cdot}HOPr$: [23519-77-9], highly flammable, moisture sensitive. Toluene: [108-88-3], highly flammable, minor toxicity. All moisture-sensitive starting materials must be handled under inert atmosphere or in a hood. Wear protective clothing in order to prevent skin

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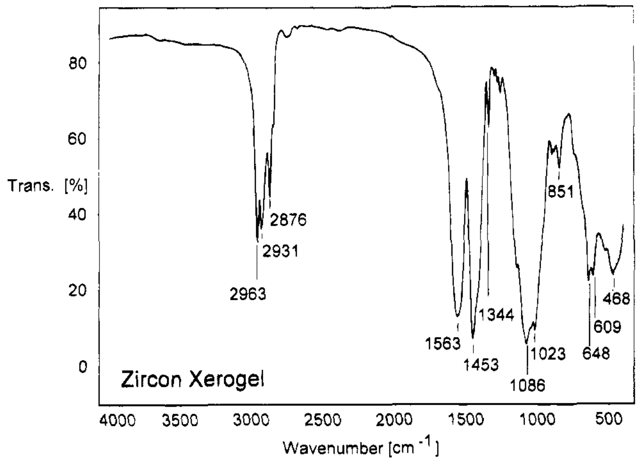

Figure 1. FTIR spectrum of the anhydrous zircon xerogel (2 mg of sample in 500 mg of KBr).

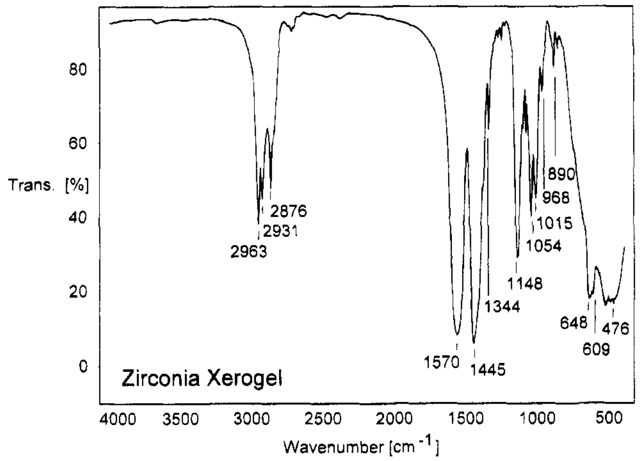

Figure 2. FTIR spectrum of the anhydrous zirconia xerogel (2 mg of sample in 500 mg of KBr).

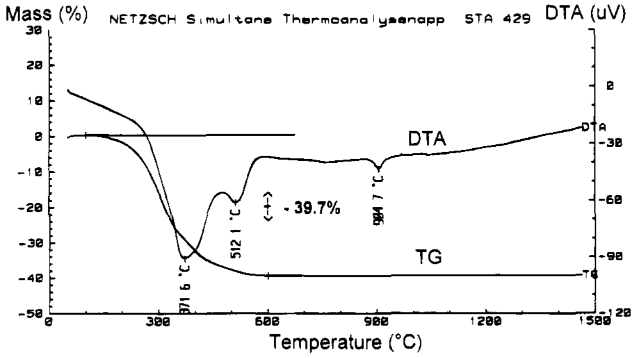

Figure 3. DTA–TGA of the anhydrous zircon xerogel (heating rate 10 °C/min; oxygen atmosphere; reference α-Al_2O_3).

and eye contact. Do not inhale dust or vapors. $ZrSiO_4$: [110771-71-6]. ZrO_2: [13-23-4].

Analytical Methods. The nonhydrolytic xerogels have been examined by TGA-DTA using a Netzsch STA 429. Samples of the gels were calcinated in an oxygen atmosphere with an increase in temperature of 10 °C/min (Figures 3 and 4).

In addition, these xerogels have been analyzed by IR spectroscopy employing a BRUKER IFS 113v FTIR spectrometer (Figures 1 and 2). Two milligrams of the respective xerogel was mixed with 500 mg of thoroughly dried KBr and pressed for FTIR examination. Preparation and measuring of the IR samples were done under inert atmosphere to exclude traces of moisture.

The raw and the calcinated nonhydrolytic zircon xerogels have also been examined by means of ^{29}Si MAS solid-state NMR using a 400 Mhz Varian Unity 400 spectrometer (standard: tetramethylsilane TMS; 79 mHz = 0 ppm, MAS frequency = 5 kHz). To eliminate the influence on the chemical shifts of the ^{29}Si atoms by unreacted organic side chains still present within the raw zircon xerogels, a sample was fired for 6 h at 550 °C in an oxygen stream to burn out the organic residues. After that treatment the sample was still amorphous (Figure 7).

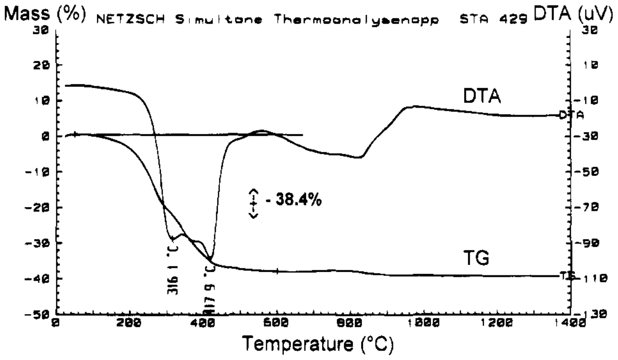

Figure 4. DTA–TGA of the anhydrous zirconia xerogel (heating rate 10 °C/min; oxygen atmosphere; reference α-Al_2O_3).

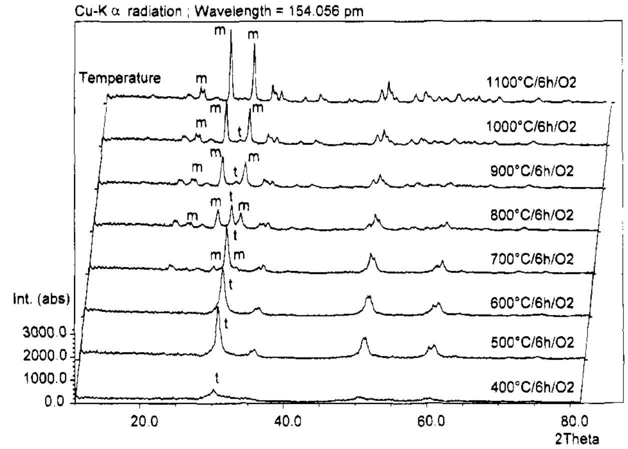

Figure 5. X-ray powder diffractograms of the calcinated zirconia gel samples, calcinated for 6 h in flowing oxygen at temperatures indicated: m, monoclinic zirconia (baddeleyite); t, tetragonal zirconia.

The calcination of the nonhydrolytic gels has been observed by X-ray powder diffractometry using a STOE & Cie, STADI P X-ray powder diffractometer. To study the crystallization of both xerogels, samples were calcinated for 6 h in a stream of oxygen covering a temperature range between 400 and 1400 °C (Figures 5 and 6).

The compositions of the calcinated gels have been determined quantitatively by EDX analyses, which were done using a Zeiss DSM 940 scanning electron microscope with 30 kV acceleration potential equipped with an EDAX PV 9800 energy-dispersive X-ray analyzer employing of the K emission lines of silicon and zirconium.

Results and Discussion

Analysis of the Molecular Condensation Products. The compositions of the liquid residues separated from the anhydrous gels were examined qualitatively by GC-MS and FTIR. Both methods confirm the presence of the expected *n*-propyl acetate, which proves that the postulated condensation reaction has occurred. Besides the ester, no other reasonable condensation products such as di-*n*-propyl ether and acetic anhydride could be detected. In contrast to the nonhydrolytic sol–gel process presented by Corriu et al.,[4] who detected the

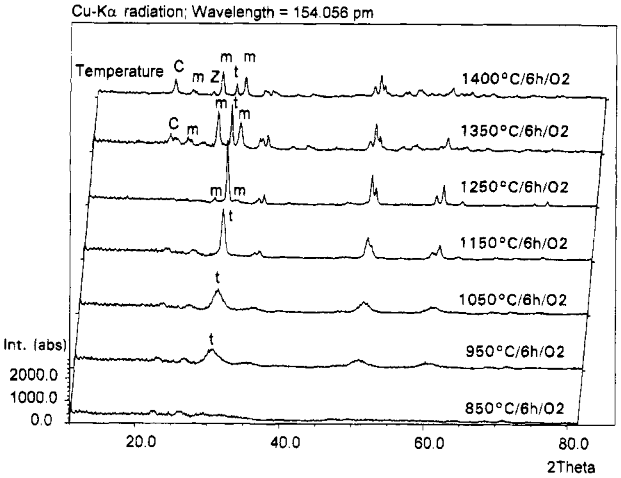

Figure 6. X-ray powder diffractograms of the calcinated zircon gel samples, calcinated for 6 h in flowing oxygen at temperatures indicated: m, monoclinic zirconia, t, tetragonal zirconia; Z, zircon $ZrSiO_4$; C, cristobalite ($c\text{-}SiO_2$).

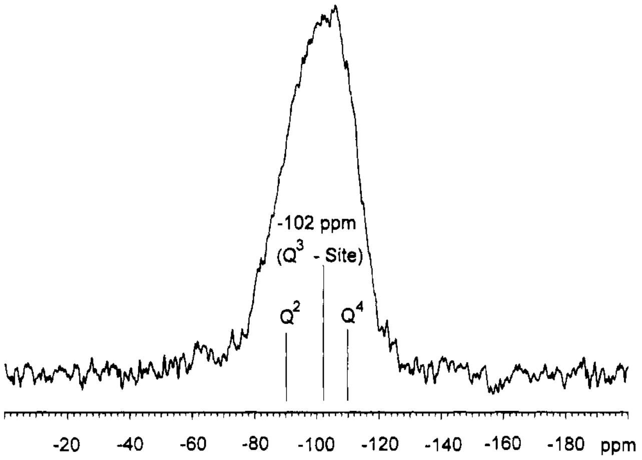

Figure 7. ^{29}Si solid-state MAS NMR of a calcinated zircon gel sample (fired for 6 h at 550 °C in an oxygen atmosphere). Standard: tetramethylsilane (TMS); MAS frequency = 5 kHz.

formation of isopropyl halides during the condensation reaction of metal halides with metal *n*-propoxides, we did not find that isopropyl acetate had been formed. The occurrence of a rearranged product led Corriu[4] to the conclusion that during this condensation reaction a carbenic cation had to be an intermediate species in a kind of SN_1-type reaction. The lack of a rearranged product in our process suggests a different mechanism without intermediate carbenic cations.

Analysis of the Anhydrous Xerogels. The anhydrous xerogels have been examined by FTIR and thermal-analysis methods. The FTIR-spectra (Figures 1 and 2) prove that neither water and hydroxo-groups nor traces of toluene and carboxylic acid ester are present in the xerogels after the drying procedure, indicated by the absence of all the characteristic and clearly recognizable absorptions of these compounds. This supports the conclusion that no volatile substances had remained in the xerogels.

To determine the rate of the condensation reaction, the amount of unreacted organic side chains within the xerogels had to be analyzed by thermogravimetry.

The zircon gels lost an average of 39.4% of their masses during this procedure (Figure 3). The weight losses end at about 550 °C, yielding a product with a defined composition [$ZrO_2{\cdot}SiO_2$ or $ZrSiO_4$; M = 183.32] confirmed by EDX analyses. Taking in account the average weight loss of 39.4% during calcination the molecular weight of the raw zircon xerogel is determined to be 302.51 g/mol. Subtracting this value from the sum of the molecular weights of the starting compounds [M ($Si(OAc)_4$) = 264.1; M ($Zr(OPr^n)_4$) = 327.22] provides the weight loss that occurs during the condensation (gelation) process. It is 288.8 g/mol of each starting compound. Because no other condensation products besides n-propyl-acetate (M = 102) could be detected, this weight loss can be credited exclusively to the formation of this ester. That implies the formation of 2.83 mol (z = 2.83 → 13) of ester/mol of each starting compound. This is 71% of the maximum amount, which is 4 mol of ester/mol of each starting compound when condensation is 100% complete (eq 13).

That simple calculation shows that 71% of the originally existing organic substituents in the starting compound materials had formed ester molecules generating Si−O−Zr bridges. This leads to an overall stochiometry for the anhydrous zircon xerogels of $ZrSiO_{2.83}(OAc)_{1.17}(OPr^n)_{1.17}$.

An analogous calculation was done for the anhydrous zirconia xerogels which lost an average of 38.5% of their masses at temperatures below 500 °C (Figure 4). This implies that 62% of the originally present organic substituents reacted during the condensation (eq 12) giving ester and Zr−O−Zr bridges. Thus, the average overall composition of the anhydrous zirconia xerogels deduced from the DTA/TG data is $ZrO_{1.24}(OAc)_{0.76}(OPr^n)_{0.76}$.

Besides other similarities the FTIR spectra of both anhydrous xerogels (Figures 1 and 2) clearly have one common feature. Both show two strong absorptions at about 1570 and 1450 cm^{-1}. According to Doeuff et al.,[19] these absorptions indicate the presence of bridging acetate groups. Both spectra do not contain any absorption bands typical for nonbridging or nonchelating acetate substituents connected to single metal atoms, normally appearing at about 1720 cm^{-1}. This is a clue that prior to the condensation reaction acetate bridges between the acetate compound and the zirconium tetra-*n*-propoxide are formed. This leads to a kind of preorganized transition complex which might be prerequiste for further reaction steps finally generating the M′−O−M bridges and the ester coproduct. However, the detailed mechanism is subject to speculation, so far.

The FTIR-spectra (Figures 1 and 2) differ significantly only in the range between 1200 and about 700 cm^{-1}. The absorption in the spectrum of the anhydrous zircon xerogel (Figure 1) at 851 cm^{-1} can be related to Zr−O−Si bridges.[11]

It is missing in the spectra of the zirconia xerogel (Figure 2). Both spectra resemble each other in the range of wavelengths below 650 cm^{-1}. The absorptions at 648 and 609 cm^{-1} are credited to Zr−O−valence vibrations, and the absorption around 470 cm^{-1} is caused by a Zr−O−Zr vibration.[15] The intensity of the absorption band at 851 cm^{-1} assigned to Zr−O−Si bridges formed by heterocondensation is quite low compared to that around 470 cm^{-1} assigned to Zr−O−

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Zr bridges formed by homocondensation. The appearance of these absorptions in the zircon xerogel spectrum indicates that besides the expected and desired Zr−O−Si bridges there are also Zr−O−Zr bridges present in the gel network and that homocondensation seems to be favored over heterocondensation due to rapid ligand exchange reactions between tetravalent (semi-) metal alkoxides and acetates (eq 16). Despite of some heterocondensation taking place during gelation the desired perfect alternation of zirconium and silicon atoms in the gel network has not been achieved.

$$\mathrm{Zr(OPr}^n)_4 + \mathrm{Si(OAc)}_4 \rightarrow \mathrm{Si(OAc)}_{4-x}(\mathrm{OPr}^n)_x + \mathrm{Zr(OPr}^n)_{4-x}(\mathrm{OAc})_x \quad (16)$$

Calcination of the Anhydrous Gels. The zirconia gels (Figure 5) start to crystallize at about 400 °C forming the tetragonal phase. At increasing the temperature to above 700 °C the monoclinic phase (baddeleyite) emerges. The amount of m-ZrO_2 increases at the cost of t-ZrO_2 with rising temperature finally yielding 100% monoclinic ZrO_2 at 1100 °C. A corresponding study of the crystallization of zirconia gels obtained by acid-catalyzed hydrolysis of zirconium-acetate by Xiaoming and Johnson[20] points out that the genesis of crystalline phases from hydrolytic zirconia gels resembles our findings for nonhydrolytic zirconia gels.

The anhydrous zircon gels, despite having an atomic scale homogeneity, do not form $ZrSiO_4$ at the moderate temperatures expected (Figure 6). The gels remain amorphous up to 900 °C. This phenomenon, also occurring in other equimolar Zr/Si systems, was previously discussed by Campaniello.[21] The formation of zirconia and zircon in nonequimolar Zr/Si systems was studied recently by Acosta.[22] The first crystalline phase appearing at temperatures above 900 °C is again tetragonal zirconia, which is transformed into monoclinic zirconia at temperatures above 1250 °C. The first traces of zircon are observed after calcinating for 6 h at 1400 °C. Firing a sample at 1400 °C for 24 h yields 100% zircon. Crystalline phases of SiO_2 (cristobalite) can only be detected at elevated temperatures exceeding 1350 °C. At lower temperatures all SiO_2 remains amorphous. The compositions of all calcinated zircon gel samples were examined by EDX which in all cases have confirmed an equimolar Si/Zr ratio.

^{29}Si Solid-State MAS NMR of the Anhydrous Zircon Xerogels. A sample of the raw anhydrous zircon xerogels was analyzed by ^{29}Si MAS solid-state NMR. This method should reveal the extent of Si−O−Zr bridges within the gel network. The ^{29}Si MAS NMR spectrum shows a broad structured signal centered at −100 ppm. This signal contains three different maxima at −90, −97, and −103 ppm. This may be attributed to the presence of at least three differently coordinated Si atoms within the raw xerogel. The ^{29}Si MAS NMR spectrum of a calcinated sample of the zircon gel (Figure 7) features a broad distribution of chemical shifts centered at −102 ppm with a half-width of 13 ppm. According to Corriu et al.[4] and Walther et al.,[23] the latter studied the SiO_2/TiO_2 system, this provides information about the extent of Si−O−Zr bridges within the gel network. Our ^{29}Si MAS NMR spectrum (Figure 7) happens to be very similar to that presented by Corriu et al. so that we can come to an analogous interpretation.[4] The shifts around −102 ppm are credited to so called Q^3 sites (one next-adjacent Zr atom to a Si atom) whereas the shifts around −90 ppm are related to Q^2 sites (two next-adjacent Zr atoms to a Si atom), and finally the shifts around −110 ppm are connected to Q^4 sites (no next-adjacent Zr atoms). The Q^2 and Q^3 sites indicate that in the reaction mixture a certain degree of heterocondensation is taking place, but that the goal of obtaining a gel network with perfectly alternated metal atoms is not achieved at all. This happens because of the occurrence of ligand exchanges between the starting materials prior to the condensation reaction step, leading to homocondensation and confirming the conclusions made on the basis of the FTIR spectra. To decrease the probability of homocondensation between silicon containing molecules and to increase the number of Q^1 and Q^2 sites, anhydrous nonequimolar ZrO_2−SiO_2 gels obtained by reaction of $Zr(OPr^n)_4$, $Zr(OAc)_4$, and $Si(OAc)_4$ with Si/Zr ratios smaller than 1 are currently under investigation.

Conclusion

In conclusion, our sol−gel process may offer a simple nonhydrolytic access to a variety of multinary oxide gels and ceramics besides the two mentioned in this paper, avoiding some complications of the conventional hydrolytic method. Through the utilization of the general method of direct condensation between (semi-) metal alkoxides and carboxylates a variety of gel compositions may be obtained, leading to pure (multicomponent) oxide gels which can be processed into (multinary) oxide ceramics. The organic residues within these anhydrous gels can be removed quite easily, positively affecting the purity of the oxide ceramics, derived from them.

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