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The self-catalytic role of zirconium *n*-propoxide in sol–gel syntheses of ZrO_2–SiO_2 mixed oxides

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The self-catalytic role of zirconium *n*-propoxide (ZP) has been investigated with respect to the synthetic parameters of ZrO_2–SiO_2 binary gels. It is found that gelation time can be shortened with a high concentration of tetraethoxysilane (TEOS) in the presence of a small amount of ZP. There are two different gelation regions depending on the amount of water added. When ZP is prehydrolyzed, the gelation time is prolonged, resulting in a more transparent gel. Based on the amount of water consumed, it is known that the hydrolysis is a relatively fast process for the ZP–TEOS sols. The mixing level of calcined binary metal oxides has been investigated by FTIR. A linear correlation between the mixing level and metal content holds up to 50 mol% of ZrO_2 under the studied conditions. For a low Zr content system, the mixing level of the metal oxides is almost independent of water concentration, whereas for a higher Zr content system, high water concentration is beneficial to the formation of Zr–O–Si hetero-linkages. On the basis of the synthetic data, a mechanism for the ZP-catalytic reactions has been proposed. Condensation rates of hydrolyzed products are addressed and their effect on the gel homogeneity and oxide mixing level are also discussed.

Introduction

In the last two decades, the sol–gel technique in relation to materials chemistry has been extensively investigated and employed to explore new approaches in obtaining oxide materials with improved properties.[1–16] Among its many advantages, the sol–gel approach is basically a low-temperature process and related chemical reactions in terms of hydrolysis and condensation can involve more than one precursor (typically metal alkoxides) and different additives, such as functional organic compounds and inorganic salts.[14–16] Hence, it is particularly suitable for synthesis of multi-component oxide materials such as optical glasses,[1–4] mixed oxides/composites,[5–7] and organic–inorganic hybrid materials.[8–10]

Incorporation of ZrO_2 into a SiO_2 matrix is known to improve the chemical resistance to alkaline attack,[3,11] fracture toughness,[12] and the surface acidity of the materials.[5,6] Compared with conventional ceramic techniques, the sol–gel method is the prevailing preparative approach for this class of materials at low temperature.[2–4,6,7] As reported,[2–4,6] when reacting tetraethoxysilane (TEOS) and zirconium *n*-propoxide (ZP), prehydrolysis of TEOS is usually required to match the reaction rates of ZP in sol–gel transformations. In these cases, however, the extent of prehydrolysis of TEOS can be influenced by a number of factors such as type and concentration of catalyst (acid or base is required), concentration of water, time of prehydrolysis and type of solvent.

Very recently, we synthesized ZrO_2–SiO_2 oxides *via* an acid/base free approach.[17] It was found that addition of a small amount of ZP could lead to fast cogelation of the binary sols in the absence of any acid or base catalyst. Using this simple synthetic route, highly mixed ZrO_2–SiO_2 oxides with ZrO_2 contents up to 30 mol% have been prepared. The cogelation phenomenon is believed to be due to interactions between the two precursors (ZP and TEOS) in the sol and is attributed to a self-catalytic effect due to the presence of ZP, but a detailed investigation on cogelation parameters was not conducted.

In the present paper, we report a synthetic investigation into the above non acid/base cogelation process, aiming at a preliminary mechanistic understanding of the self-catalytic effect. Through examining synthetic parameters, chemical interactions between ZP and TEOS have been explored. Although it is difficult to obtain a complete kinetic picture for the material synthesis at the current stage, the correlation between gelation time and the two precursor compounds reveals major kinetic factors in the cogelation process. Together with FTIR studies of water consumption and Zr–O–Si hetero-linkage formation, the observed self-catalytic effect can be explained by two synthetic approaches designed.

Experimental

Tetraethoxysilane (TEOS, purity > 98%) and zirconium *n*-propoxide (ZP, 70 wt% in *n*-propanol) were obtained from Fluka and Aldrich, respectively. Acetylacetone (acac, 99.5%) and isopropanol (99.7%) were obtained from Merck. The synthetic procedure for mixed ZrO_2–SiO_2 gels was developed from that used previously for ZrO_2.[13,15] It should be stressed that, unlike other preparative methods reported,[2–4,6] no acid or base catalyst was used in the current work.

Two different synthetic methods (one-step and two-step) were employed in the ZrO_2–SiO_2 mixed oxide synthesis. A typical preparation procedure for the one-step method can be described as follows: as-received ZP–*n*-propanol solution was diluted to the desired molar concentration in pre-mixed isopropanol–acac under vigorous stirring in a glove box. Here acac was used as a chelating agent to stabilize ZP; the molar ratio of acac to ZP was kept at 1 in all experiments. The desired amount of TEOS was added to the above solution and the mixture stirred continuously for 15 min. Hydrolysis was then initiated by adding deionized water. The preparative beaker was sealed with a plastic film to prevent chemical/solvent evaporation. The gelation time (t_g) was determined for various mixed sols and was measured from the moment of water addition until the sol lost its fluidity. Usually, after adding water, the sol was stirred for a further 10 to 15 min and then allowed to stand. The second method is quite similar to the first, except that prehydrolysis of ZP–acac was carried out (*i.e.* the total water required for the gel system was added at this point) before adding TEOS. In such cases, the gelation time t_g was measured from the moment of TEOS addition (Table 1).

The value of t_g reported was taken from an average of 2 or 3 repeated experiments. The obtained wet gels were further aged for one week at room temperature before drying at 80 °C for 48 h. The dried gels were then crushed into powders and stored in sample bottles for further use. Calcination of the gels was carried out by heating at a rate of 4 °C min^{-1} (the same rate was used during cooling) to 500 °C and kept at the same temperature for 4 h before cooling.

Sol solutions during the hydrolysis and the powdered gels after heat-treatment at 500 °C were investigated with Fourier transform infrared spectroscopy (FTIR; FTS135, Bio-Rad). A KRS cell with a wall thickness of about 0.1 mm was used to house the solutions while the potassium bromide (KBr) pellet technique was employed to hold the powdered gels (1 wt%). Each FTIR spectrum was collected after 100 scans with a resolution of 2 cm^{-1}.

Results

t_g and concentrations of ZP and TEOS for the one-step process

In our previous work,[17] gelation times (t_g) of single component alkoxide sols (either ZP or TEOS) were compared with those of ZP–TEOS mixed sols (double component alkoxide sols). Based on the observations that the single component alkoxide sols did not transform into gels, even after three months, but the mixed sols were able to transform into stiff gels in less than 200 min, a cogelation process between ZP and TEOS was deduced.[17] In this work, the cogelation phenomenon will be further explored.

Fig. 1 shows the dependence of t_g on precursor concentrations, varied in the ranges 0.2–0.5 and 0.25–1.0 M for ZP and TEOS, respectively. The concentration of water was kept at 4.0 M in these experiments, which was in the middle of the theoretical range (1.8–6.0 M) required for complete hydrolysis of all the alkoxides:

$$M(OR)_4 + 4H_2O \rightarrow M(OH)_4 + exROH \quad (M = Zr \text{ or } Si) \quad (1)$$

It is noted that the wet gels obtained are transparent or semi-transparent with obvious elasticity; they are typical polymeric gels. For example, the gel prepared with 0.25 M TEOS and 0.5 M ZP is clearly transparent, whereas the transparency of the wet gels reduces gradually with decreasing ZP concentration or increasing TEOS concentration.

It can be seen that t_g decreases with increasing TEOS concentration, but increases as the concentration of ZP increases. This phenomenon was observed for the first time in our previous study, in which the molar ratio of ZP to (ZP+TEOS) was varied while the total concentration of ZP plus TEOS was kept constant.[17] Hence, with increasing ZP molar concentration, the concentration of TEOS decreases and this leaves an uncertainty as to the effect of TEOS concentration on t_g. As shown in the current work (Fig. 1), the cogelation process is unambiguously confirmed. In general, the gelation process is faster with a higher concentration of TEOS and a lower concentration of ZP under the studied conditions.

Table 1 Effect of prehydrolysis of ZP–acac on gelation time (t_g) of mixed ZP–TEOS sols

Prehydrolysis of ZP/h	t_g/min
0	36
1	47
5	57
20	65
67	75

Composition of the sol. [ZP] = 0.2 M, [acac] = 0.2 M, [TEOS] = 1.0 M and [H_2O] = 4.0 M.

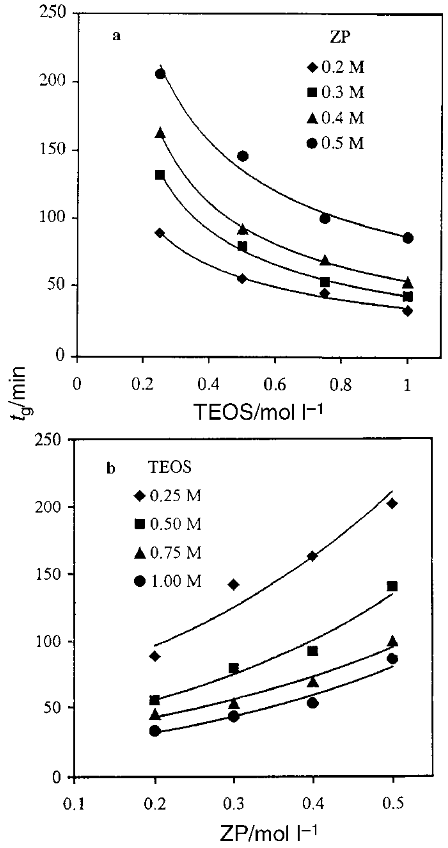


Fig. 1 Gelation time (t_g) of ZP–acac–TEOS–isopropanol–water mixed sols as a function of the molar concentrations of TEOS (a) and ZP (b); note that the molar ratio of acac/Zr = 1 and [H_2O] = 4.0 M.

t_g and concentration of water for the one-step process

Fig. 2 shows the dependence of gelation time t_g on the concentration of water added in various sols. With a 1.0 M concentration of water, the sol cannot be transformed into a gel in less than one week. However, t_g decreases with increasing water concentration. For each set of experiments, a sharp drop in t_g is observed from which a turning point can be interpolated. Clearly, there are two different gelation regions (slow and fast) divided by the turning points.

Furthermore, the turning point apparently depends on sol composition. Keeping TEOS at constant concentration (0.5 M) while changing that of ZP (0.1–0.5 M), the turning point shifts from *ca.* 2.0 M to *ca.* 4.0 M [Fig. 2(a)]. By contrast, with a constant ZP concentration [0.2 M, Fig. 2(b)], the turning point does not move at all even when the TEOS concentration is changed from 0.5 to 1.5 M. These results indicate that the turning point is determined by the concentration of ZP, not by that of TEOS.

It is noted that the concentrations of water at these turning points are significantly higher than the theoretical amounts required for complete hydrolysis of ZP. On the basis of these data, roughly speaking, a water content 2 to 4 times higher than the theoretical value allows a slow gelation process to switch to a high-speed one.

t_g and preparation parameters for the two-step process

It is known that the hydrolysis of TEOS, compared with that of ZP, is extremely slow in the absence of acid or base catalysts. Hence, it is thought that the above cogelation may result from hydrolysis of the ZP–acac complex and then from reactions between the prehydrolyzed ZP–acac and TEOS. To verify this hypothesis, the two-step experiments were conducted, which allow ZP to react with water (*i.e.* hydrolysis and condensation)

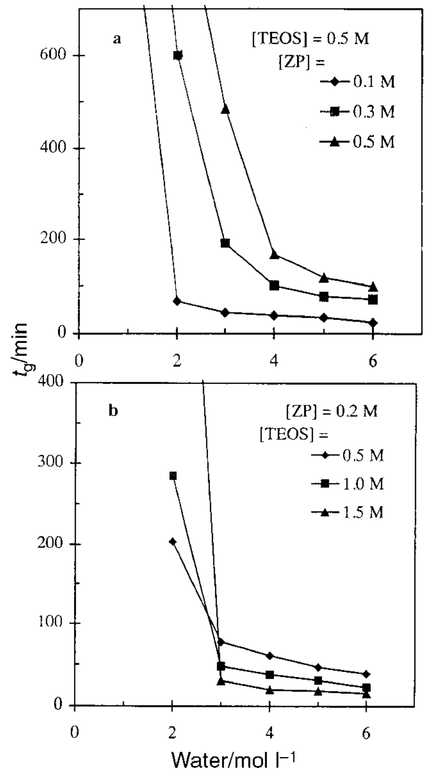


Fig. 2 Gelation time (t_g) of ZP–acac–TEOS–isopropanol–water mixed sols as a function of molar concentrations for (a) [TEOS] = 0.5 M and (b) [ZP] = 0.2 M; note that the molar ratio of acac/Zr = 1.

for a certain period of time before addition of TEOS (see Experimental section).

This two-step procedure also produced polymeric gels similar to those obtained from the one-step process. As shown in Table 1 however, the gelation time t_g increases with increasing ZP–acac pre-reaction time, for example, 35 min for a one-step process and 75 min for a two-step process with a pre-reaction time of 67 h. The transparency of gels obtained from the two-step process increases slightly with increasing pre-reaction time (Table 1). This may be attributed to slower hydrolysis/condensation reactions in the two-step process, because pre-reacted ZP–acac is less catalytically active.

The similarity of the products prepared *via* one-step and two-step processes suggests that the reactions involved in the two preparative methods proceed in a similar fashion. With the two-step method, hydrolysis and condensation of ZP–acac takes place in the first step, resulting in various hydrolyzed monomers and oligomers. When TEOS is added, a fast gelation process occurs to form a mixed binary gel. A similar reaction route may occur under the one-step conditions, *i.e.* hydrolysis of ZP–acac takes place first, followed by reactions between the prehydrolyzed ZP species and TEOS. The proposed mechanism was confirmed by FTIR spectroscopy.

FTIR investigation into the hydrolysis of ZP and TEOS

In order to understand the chemical interactions between ZP and TEOS in the mixed sols we measured the amount of water consumed by the chemical reactions, which is an important indicator that can be determined by means of IR spectroscopy. In particular, a band at 1640 cm^{-1} (molecular bending mode of water) was employed. This band has been used for quantitative analysis of water in organic solvents when it is not obscured by other bands due to the solvent.[18,19] For instance, it has been utilized in a similar sol system, consisting of TEOS and TP (titanium isopropoxide) chelated with acac (*i.e.* TP–acac), to monitor the water content.[18] It was found that the IR data on water consumption were in accordance with those obtained by the means of the Karl–Fischer method.[20]

FTIR spectra of TEOS–solvent (isopropanol), ZP–acac–solvent, and ZP–acac–TEOS–solvent sols with various water additions are shown in Fig. 3. As can be seen, the molecular water band appears at around 1640 cm^{-1} and its intensity increases with the amount of water added. In addition to the weak band at 1640 cm^{-1} for water, the strong double peaks at 1600 and 1530 cm^{-1} in Fig. 3(b) and (c) are characteristic of a ZP–acac complex.[21,22] The areas of the bands due to water were integrated and correlated with the amount of water added, as reported in Fig. 4. In the TEOS–solvent case, the 1640 cm^{-1} band can be clearly seen, even with a small amount of water (H_2O/TEOS = 0.2); the band area increases linearly with the amount of water added. This is because hydrolysis of TEOS is very slow under non-catalytic conditions.[23] While the molecular water absorption modes can be detected when H_2O/ZP $\geqslant 2$ for the ZP–acac–solvent, and H_2O/ZP $\geqslant 3$ for the ZP–acac–TEOS–solvent systems, the areas of the water bands are nevertheless small. This observation indicates hydrolysis of the precursor systems. In particular, the consumption of water in the ZP–acac–TEOS–solvent sol is significantly higher than that of the ZP–acac–solvent. It follows from Fig. 3 and 4 that the hydrolysis of TEOS is accelerated in the presence of ZP, since the water consumed is direct evidence for the hydrolysis.

It should be mentioned that the first spectrum of each sol was taken 10–15 min after addition of water (*i.e.* reaction

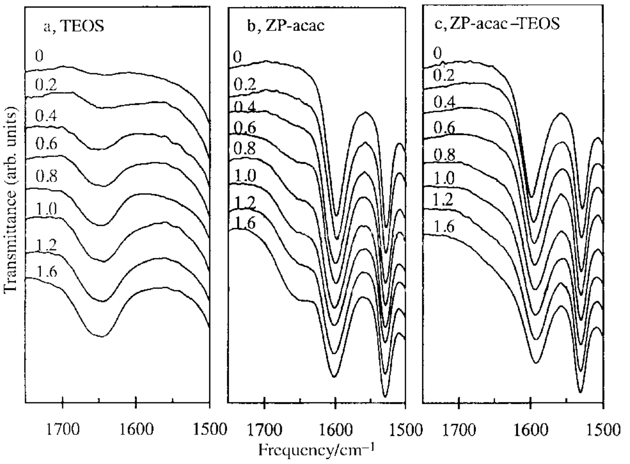


Fig. 3 FTIR spectra of various mixed solutions with different molar concentrations of water (in M, values noted in the Figure): (a) TEOS–isopropanol–water, (b) ZP–acac–isopropanol–water and (c) ZP–acac–TEOS–isopropanol–water; in all solutions [TEOS] = 1.0 M, [ZP] = 0.2 M and the molar ratio of acac/Zr = 1.

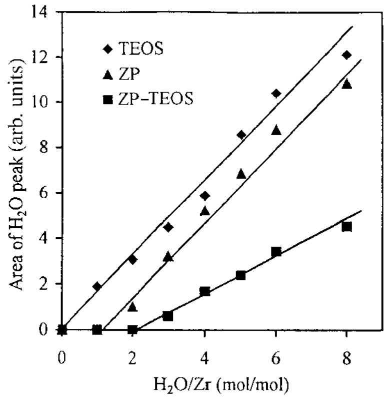


Fig. 4 The correlation between the peak area of the 1640 cm^{-1} IR band of water molecules in the three solution systems [reported in Fig. 3 (a) to (c)] and the initial concentration of water added.

time = 10–15 min, shown in Fig. 3), and after which, further spectra were recorded continuously. Within the studied range of 10–60 min, the intensity of the water band for each sol did not change with respect to reaction time. For example, band areas for reaction times of 10–15 min and 60 min are essentially the same. This observation indicates that the hydrolysis is a relatively fast process; it was complete before our FTIR spectra were measured [Fig. 3(c)].

FTIR characterization of the oxide mixing level

It has been documented that the Si–O–Si stretching band[24,25] near 1100 cm^{-1} will shift towards lower values when Zr atoms replace the Si atoms to form Si–O–Zr hetero-linkages.[6,17,26–29] As demonstrated in our previous work,[17] this red-shift of the IR band is proportional to the population of the hetero-linkage in binary oxides of ZrO_2–SiO_2. All the xerogels described in Fig. 1 were heat-treated at 500 °C for 4 h and then examined by FTIR. Absorption band values of the Si–O–Si or Si–O–Zr stretching modes are plotted against the molar content of Zr. As reported in Fig. 5, the red-shifts of the 1100 cm^{-1} band for most samples fall on a linear line.

It was found in our previous work that with acac/Zr = 0.2 to 0.4 the linear relationship between the red-shift of the 1100 cm^{-1} band and Zr content extends up to 50 mol% of Zr. However, with acac/Zr = 1.0 and Zr content $\geqslant$30 mol%, the red-shift is generally small and the linear relationship does not hold, suggesting that some of the Zr atoms are not involved in the formation of hetero-linkages.[17] Since all the gels were prepared with acac/Zr = 1.0 in the current work, it seems that the linear relationship can be further extended up to 50 mol% of Zr. This discrepancy is believed to be due to a higher concentration of water employed (4.0 M in this work, compared to 2.5 M in ref. 17). The influence of water concentration on the mixing level of ZrO_2–SiO_2 is shown in Fig. 6. Apparently, for a lower Zr content [ZP/(ZP + TEOS) = 11.8 mol%, curve B], the mixing level is roughly independent of water concentration, but for a higher content [ZP/(ZP + TEOS) = 37.5 mol%, curve A], higher water concentration is beneficial to the formation of the hetero-linkages.

Discussion

Hydrolysis of TEOS and ZP

Mechanisms for the hydrolysis and condensation of TEOS have been extensively investigated using various techniques, including ^{29}Si NMR.[23,30] It has been well documented that the hydrolysis of TEOS is very slow in a neutral alcoholic solution and thus an acid or a base is needed to catalyze the reaction in the synthesis of SiO_2 gel. With an acid catalyst, oxonium ions (H_3O^+) attach electrophilically to the oxygens of alkoxy groups (protonation), which makes the Si atoms highly prone to nucleophilic attack by water. With a base catalyst, a hydroxide ion (OH^-) nucleophilically attacks a positively charged Si atom. Unlike silicon alkoxides (TEOS and TMOS), most transition metal alkoxides, including ZP, are so reactive that special care must be taken to prevent direct hydrolysis by moisture. The vast difference in hydrolysis reactivity between $Si(OR)_4$ and transition metal alkoxides has been addressed in the literature using a Partial Charge Model (PCM).[8] Accordingly, the reactivity between $M(OR)_4$ (M = metal) and HOX (X = H or R) depends mainly on the electrophilic power [determined by partial charge δ(M)] and the unsaturation of the metal atom (determined by $N-Z$, where N and Z are the usual coordination number and oxidation state of the metal respectively). Due to its low electronegativity, the silicon atom in TEOS has a relatively low electrophilic power [$\delta(Si) = 0.32$ and $N-Z = 0$].[8] This low value of δ(M) and zero value of $N-Z$ make TEOS fairly stable against hydrolysis in comparison to transition metal alkoxides such as $Zr(OPr)_4$, used in the current case [$\delta(Zr) = 0.65$ and $N-Z = 2$ to 4], and $Ti(OEt)_4$ [$\delta(Ti) = 0.60$ and $N-Z = 2$].[8]

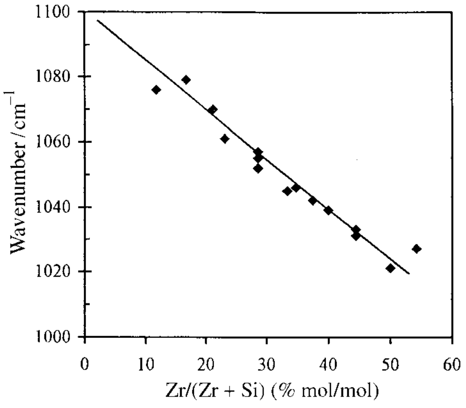


Fig. 5 Wavenumber plot for the IR band due to the Zr–O–Si stretching vibration against ZrO_2 molar content in the calcined gels; all the samples were calcined at 500 °C for 3 h before IR measurement.

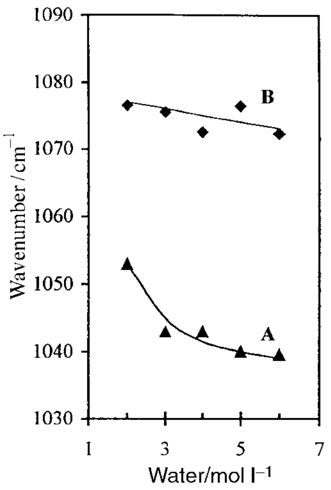


Fig. 6 Wavenumber plot for the IR bands due to the Zr–O–Si stretching vibration against water concentration in the gel preparation: (A) [ZP] = 0.3, [TEOS] = 0.5, acac/Zr = 1 and (B) [ZP] = 0.2, [TEOS] = 1.5, acac/Zr = 1; all the samples were calcined at 500 °C for 4 h before IR measurement.

As a result of its low hydrolysis reactivity, prehydrolysis of TEOS is usually applied in the presence of a catalyst (acid or base) before addition of the second metal alkoxide to achieve a better mixing level for the binary oxides.[2–4,6] This prehydrolysis technique was established based on the view that there is no chemical interaction between the two alkoxide precursors in the early stages of the reactions, *i.e.* the precursors undergo hydrolysis separately.

Catalytic role of ZP in TEOS hydrolysis

As revealed in Fig. 1, the gelation time t_g of the mixed sols decreases profoundly with increasing TEOS concentration. This result indicates that TEOS is directly involved in construction of the gel network, leading to a much shorter gelation time, compared to the mono-component reaction.

The cogelation phenomenon due to the presence of a second alkoxide precursor was also reported for the TEOS–TEOG (tetraethoxygermanate) system.[31–33] The addition of TEOG to a prehydrolyzed TEOS sol results in a decrease of t_g and this effect is more pronounced with increasing TEOG concentration up to 50 mol%.[32] The cogelation effect of

TEOS–TEOG has been attributed to the following chemical reaction:[32,33]

$$\equiv\text{Si–OH} + \text{EtO–Ge}\equiv \rightarrow \equiv\text{Si–O–Ge}\equiv + \text{EtOH} \qquad (2)$$

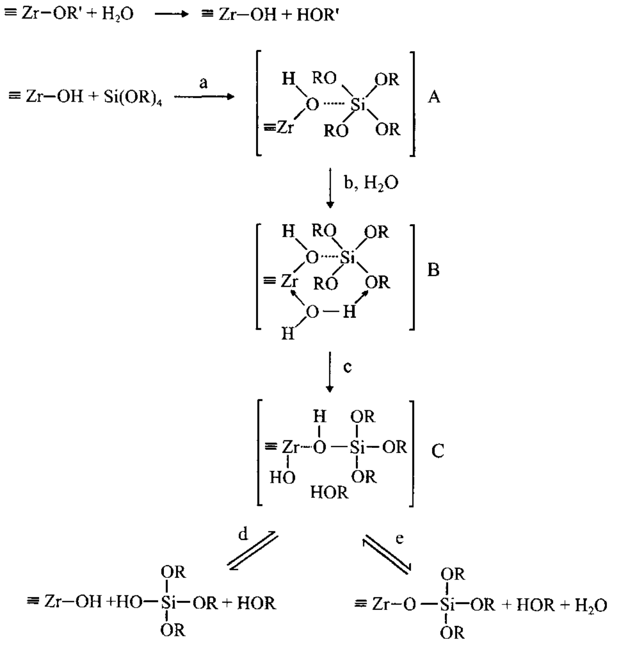
in which TEOG need not be hydrolyzed. In fact, the hydrolysis of TEOG before addition to the TEOS sol would diminish this cogelation effect. By analogy, the cogelation in the current ZP–acac–TEOS system can be attributed to:

$$\equiv\text{Zr–OH} + \text{EtO–Si}\equiv \rightarrow \equiv\text{Zr–O–Si}\equiv + \text{EtOH} \qquad (3)$$

This reaction was used to explain the formation of Zr–O–Si hetero-linkages in our preliminary work.[17] However, eqn. (3) alone is obviously not enough to account for the rather complex effect of ZP on t_g. From our new IR data, it can be seen that the hydrolysis of TEOS in the mixed sols takes place within minutes, as reported in Fig. 3(c). Considering the fact that the hydrolysis of TEOS is very slow without catalysts,[23,30] ZP must play an important role in these cases. A tentative mechanism for the reaction is proposed in Scheme 1 to explain the large water consumption observed in the ZP–acac–TEOS system [Fig. 3(c)].

According to this reaction scheme, the ZP–acac is first hydrolyzed upon addition of water, resulting in Zr(acac)(OPr)$_{4-x}$(OH)$_x$ species which are very stable owing to the strong chelating effect of the acac molecules.[8,19,34–36] The hydrolyzed ZP species interacts with TEOS through its hydroxyl group, leading to a bimolecular complex A. Since the Zr centre in ZP has the capacity to increase its coordination number (up to 8, as in its oxide), a water molecule can then react with this complex and convert it into an intermediate complex B, which then decomposes to provide the intermediate C. Compound C may react *via* one of two routes (d and e) to afford the final products. Apparently, route d is a typical catalytic process because the Zr–OH species is regenerated. In this way, the hydrolysis of TEOS is catalyzed by the initially formed Zr–OH species.

Formation of Zr–O–Si alkoxide complexes from ZP and TEOS in alcohol–water–acid solution has been reported.[37,38] Using small angle X-ray scattering, it was found that a linear polymer/complex, ≡Si–O–Zr–O–Si≡, was formed in the sol with ZP/TEOS = 0.5 in the presence of HCl.[37] If route e, which leads to Zr–O–Si hetero-linkages, is predominant, the ≡Zr–OH species will be consumed over the course of the reaction and the hydrolysis of TEOS (route d) will then be suppressed. In other words, a high concentration of ZP would be beneficial to route e. Nonetheless, in our previous study it was observed that a fairly low ZP concentration [ZP/(ZP + TEOS) = 2–5 mol%] favors the gelation of TEOS. Together with the new evidence in Fig. 1 to 4, we believe that the catalytic route d is predominant under the current reaction conditions, especially when the ZP concentration is low.



Scheme 1 Proposed mechanism for catalytic cogelation reactions between TEOS and ZP–acac in the presence of water.

According to the results in Fig. 2, a high $H_2O/(ZP + TEOS)$ molar ratio is necessary for fast gelation. When the water concentration is below the turning point, the gelation process becomes very slow. This is probably because the ≡Zr–OH species are consumed during the formation of hetero-linkages at low water concentration (route e). Based on this observation, it is proposed that there is an equilibrium between route d and route e, which is determined by the concentrations of ≡Zr–OH, ≡Si–OH, ≡Zr–O–Si≡ and H_2O in the reaction mixture. It is thus reasonable to expect the equilibrium favors the catalytic route d with a high concentration of water and a low concentration of ≡Zr–OH. As shown in Fig. 2, the minimum water concentration at which route e can be effectively suppressed is about 1.6 to 2.5 M.

It should be mentioned that the acidity of Zr (a Lewis acid)[16] in the ZP complexes is important in the above catalytic processes. As shown in Fig. 1, a high Si/Zr ratio favors cogelation, which suggests that an isolated ZP species (or short oligomer) is more active than its condensed/agglomerated forms. This is further supported by the two-step synthesis reported in Table 1. For the prehydrolyzed ZP, which may result in larger oligomeric species from ZP hydrolysis/condensation, the catalytic activity of the ZP complexes on cogelation is apparently lower.

Cogelation of ZP and TEOS species

Condensation of the various hydrolyzed species in the current mixed sols can take place between the same or different metal hydroxide groups:

$$\equiv\text{Zr–OH} + \text{HO–Zr}\equiv \rightarrow \equiv\text{Zr–O–Zr}\equiv + H_2O \qquad (4)$$

$$\equiv\text{Si–OH} + \text{HO–Si}\equiv \rightarrow \equiv\text{Si–O–Si}\equiv + H_2O \qquad (5)$$

$$\equiv\text{Zr–OH} + \text{HO–Si}\equiv \rightarrow \equiv\text{Zr–O–Si}\equiv + H_2O \qquad (6)$$

Reaction (4) is very slow because a pure ZP–acac sol cannot transform into a gel, even after three months. Obviously, this is due to the strong stabilizing effect of the chelating acac ligand (not shown in the formula). In view of the slow reaction in eqn. (4), reactions (5) and (6) should proceed simultaneously and dominate the condensation process which results in gelation. In particular, when the content of ZP is small, it is expected that reaction (5) is the main reaction leading to gelation, since t_g decreases significantly with increasing TEOS concentration. When the concentration of ZP (or ≡Zr–OH) is increased, eqn. (6) becomes the dominant reaction. Compared with the gelation times shown in Fig. 1, it can be concluded that, in the presence of the ≡Zr–OH catalyst, the gelation rate in reaction (5) is faster than that in reaction (6).

Effect of synthesis conditions on homogeneity and mixing level

The transparency of a gel can be used as a rough indication for its homogeneity. As described above, the transparency (*i.e.* the homogeneity) of the wet gels obtained decreases with increasing TEOS concentration or decreasing ZP concentration. After aging for one week at room temperature and drying at 80 °C for 48 h, the order of transparency of the gels was unchanged. In addition to this, the homogeneity of the mixed gels can be improved by pre-reaction of ZP with water before addition of TEOS (two-step method).

It is known that in the one-step preparation reactions (5) and

(6) dominate the condensation process. Since reaction (5) is faster than reaction (6) oligomers or colloid particles of $(SiO_2)_n$ may form during the course of the reaction and become trapped in the matrix of the gel, a view supported by the fact that there is a distinct point (time) at which the clear sol turns opaque during the gelation process and that this phenomenon becomes more pronounced when the TEOS concentration is higher. Accordingly, the homogeneity of the gel can be improved when the TEOS concentration is decreased and the ZP concentration is increased.

Under the two-step preparation conditions the contribution of reaction (4), which produces oligomers of $[ZrO_x(OH)_{3-x}(acac)]_m$, should be considered. Because of the low condensation rate, however, these oligomers should be small in size. As indicated in Table 1, with prehydrolysis of ZP, the gelation time of mixed gels can indeed be prolonged. Since the rate of reaction (5) is now lowered, less or smaller sized $(SiO_2)_n$ particles are formed and hence higher transparency gels can be obtained.

Although the homogeneity of the wet gels obtained under different conditions varies, this variation seems not to influence the goodness of mixing level of the gels after aging, drying and finally calcining at 500 °C. As shown in Fig. 5, the linear correlation between the IR band and Zr mol% seemingly suggests that most Zr atoms are involved in the formation of Zr–O–Si hetero-linkages. As about 80 vol% of the wet gel is made up of water and/or solvents, byproducts of the condensation/hydrolysis reactions, the chemical environment around Zr atoms in the gel network may not meet full coordination conditions as found in its mono-oxide form. In particular, acac molecules may still remain attached to ZP and certain chemical reactivity among the central metal atoms still exists. During the thermal treatment, one would expect that a rearrangement of the Zr, Si and O atoms takes place, resulting in cleavage of old Si–O–Si and Zr–O–Zr bonds and formation of new Zr–O–Si linkages. This explanation is also in accordance with the result reported for the xZrO$_2$–SiO$_2$ ($x \leqslant 10$ mol%) system in which chainlike polymers of *ca.* 10 nm in length were formed at the gel point, and were transformed into oxide regions with diameter of *ca.* 16 nm after drying at 120 °C.[38]

Conclusions

In summary, using the one-step synthetic approach, it was found that the gelation time decreases with increasing TEOS concentration, but increases with increasing ZP concentration. With an increase in water content, the gelation time decreases, showing two distinct gelation regions. Generally speaking, a water content of 2 to 4 times higher than the theoretical value for hydrolysis allows a slow gelation process to switch to a high-speed one. Furthermore, the gelation time can be increased *via* a prehydrolysis of ZP (the two-step approach), which can improve gel transparency. Using the FTIR technique, it was revealed that the consumption of water in ZP–acac–TEOS was significantly higher, indicating rapid hydrolysis. For a low Zr content gel, the mixing level of the binary oxide is almost independent of water concentration, but for a higher Zr content gel, high water concentration is beneficial to the formation of Zr–O–Si hetero-linkages (up to 50 mol% of Zr). On the basis of synthetic findings, the proposed catalytic reaction scheme seems to explain well all the experimental results. We note that the condensation rate has a hierarchy of $\equiv$Si–O–Si$\equiv$ > $\equiv$Zr–O–Si$\equiv$ > $\equiv$Zr–O–Zr$\equiv$. The homogeneity of the binary oxide gels can be improved by controlling the gelation rate, which in turn can be controlled by the concentrations of TEOS and ZP and by the synthetic approach, such as the two-step method developed here.

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