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STUDY OF THE DRYING ZIRCONIA GEL-PRECIPITATES USING THERMAL ANALYSIS

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Abstract

Thermoanalytical techniques (TG, DTG, DTA and EGA) can be helpful in studying gel compositions and relating the chemical history and the role of the precipitant to the chemical properties of gels. The objective of our work was to determine the influence of the initial conditions in the reaction mixture on the product characteristics. Zirconia gels were prepared by the gel-precipitation method by the hydrolysis of zirconium tetrachloride dissolved in methanol. The substitution of water by methanol was chosen in order to obtain a reaction medium in which better control of the hydrolysis and condensation reactions of the zirconium precursor were achieved and thus also better control of the final properties of the dried zirconia gel-precipitates could be obtained. The nature of the hydrated zirconia gels obtained during the gelation process is strongly influenced by the conditions of the reaction mixture, e.g. concentration of the zirconium precursor, the mixing rate and particularly by the amount of water added. To distinguish between various types of water in the gel-precipitates, the furnace atmosphere and the partial water pressure were altered appropriately. It was shown that initial zirconium to water molar ratio has a significant effect on the properties of the final products. It was assumed that, according to the preparation conditions, three different types of water are present in the formed zirconia gel-precipitates. Modification of the dehydration processes of zirconia gel-precipitates enables control of the final microstructural and surface properties of the dried gels which are suitable for further catalysts support as well as mixed oxide preparation.

Keywords: thermoanalysis dehydration, zirconia gels

Introduction

Sol-gel processes have been shown to be an affective alternative method for the synthesis of promising homogenous and reactive solids. The most successful applications of various sol-gel processes are those that utilize the potential advantages of sol-gel processing such as purity, homogeneity, and controlled porosity with the ability to form shaped objects at low temperature [1]. Gel-precipitation techniques were widely used for the preparation of zirconia from zirconia gels with specific microstructural properties and crystalline forms [2, 3]. The high surface area of dried gels results in high reactivity which in turn permits low temperature processing. ZrO_2 with high specific surface area has been reported to be an effective catalyst support or, in some specific cases promoter, e.g. methanol formation on zirconia dioxide [4, 5]. The crucial step in the preparation of zirconia with specific

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microstructural and surface properties is the heat treatment of the zirconia gels in order to avoid the formation of large unporous agglomerates with low specific surface area [6]. Thus, an understanding of the mechanisms of mass losses during thermal treatment and subsequent crystallization of zirconia gels enables optimization process conditions. Thermoanalytical techniques in combination with chemical analysis can be most valuable in relating the chemical history and the role of gel-preparation conditions to the properties of gels, and have been used to determinate the origin of microstructure in zirconia gels [7].

The objective of this work was to determine the influence of the processing conditions of the reaction mixture on the composition and properties of the zirconia gel-precipitates obtained. The modification of dehydration of intermediate zirconia gel-precipitates changes the final microstructural and surface properties of dried gels and renders them suitable for use as catalyst supports as well for mixed oxide preparation.

Experimental

Hydrous zirconia gel-precipitates were obtained by adding gaseous ammonia (final *pH* 9) to a vigorously stirred methanol solution of zirconium tetrachloride (300 ml, 0.143*M*), to which an amount of water necessary for the hydrolysis and condensation reactions was added. To determine the influence of the amount of added water on the properties of the zirconia gel-precipitates obtained the $Zr^{4+}$to H_2O initial molar ratio in a reaction mixture was varied from 1:0.68 to 1:16.18 respectively. The obtained gel-precipitates were centrifuged off and dried under vacuum for two hours at room temperature. These intermediates were subjected to thermal analysis (TG, DTG and EGA) in a dynamic argon atmosphere saturated with water at 30°C (95.4 %vol. Ar and 4.6 %vol. H_2O, heating rates 1, 4, 10 and 20 K min^{-1}, sample weight 50 mg). Scanning electron microscopy (Jeol T-300 microscope) was used for further characterization of the samples.

Results and discussion

Gel-precipitation from a solution of zirconium tetrachloride in methanol as a reaction medium is one of the techniques for the preparation of zirconium hydrated oxide. Several parameters, such as *pH*, mixing rate, temperature, concentration and above all the initial organic solvent to water ratio must be controlled to produce satisfactory products with specific properties. The effect of the initial Zr^{4+}:H_2O molar ratio on the drying characteristics of zirconia gels is shown in Table 1 and Fig. 1. The samples of fresh zirconia gels can, according to their dehydration properties as shown in the TG curves in Fig. 1, be divided into two groups. The classification into groups is based on the initial Zr^{4+}:H_2O molar ratio. If the initial molar ratio of zirconium ions to water exceeds 1:4 value the mass loss occurs over three different stages (samples Z4, Z5 and Z6).

In this case the first stage (30–155°C) can be attributed to the evaporation of methanol and adsorbed water from the surface of zirconia gels. In this temperature interval one major DTG peak followed by a smaller or just detectable peak can be found. The first DTG peak temperatures (42.8°C in all three cases) and mass losses

Table 1 Weight losses and peak temperatures of hydrous zirconia samples during thermal analysis

Sample	Initial molar ratio Zr^{4+} to H_2O	Weight loss/ wt% and T_{peak} /°C					
		I. stage		II. stage		III.stage	
Z1	1:0.68	25.19; *84.3* (I. + II. stage)				2.98	*457.0*
Z2	1:1.18	28.46; *74.8* (I. + II. stage)				2.54	*447.0*
Z3	1:2.17	33.77; *49.2* (I. + II. stage)				1.72	*436.4*
Z4	1:4.19	28.43	*42.8*	22.76	*228.4*	2.10	*391.6*
Z5	1:8.18	28.13	*42.8*	24.04	*231.6*	1.60	*390.4*
Z6	1:16.18	27.91	*42.8*	23.94	*234.8*	1.53	*388.4*

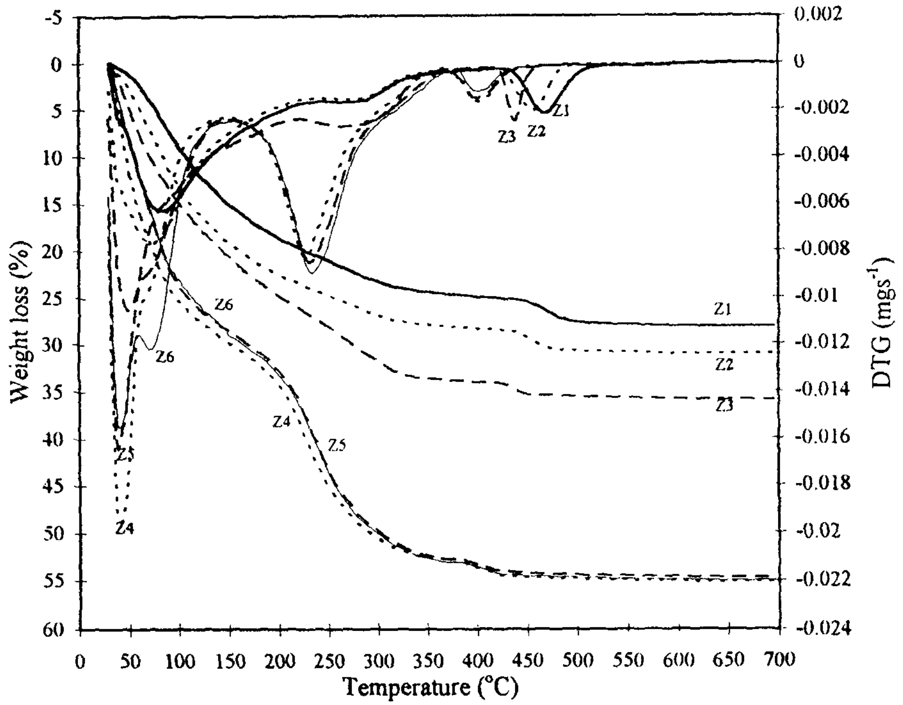

Fig. 1 Dehydration of zirconia gels followed by thermal analysis

for this step (28.43 to 27.91%) are not affected by the Zr^{4+}:H_2O molar ratio in the initial reaction mixture. However, by increasing the addition of water to the initial reaction mixture (3.24, 6.32 and 12.49 ml of water added respectively) the first dehydration stage is broadened (most pronounced for the Z6 sample). The second minimum becomes more distinctive when the water content in the initial solution is higher, indicating the presence of physically adsorbed water on the surface of drying gels.

The second stage of volatile loss occurs over a broad temperature range of 155–375°C. According to Blesa *et al.* [8] the reaction occurring at this stage can be represented as:

$$\left[Zr_4O_{(8-x)}(OH)_{2x}\cdot yH_2O\right]_n \rightarrow \left[Zr_4O_{(8-x)}(OH)_{2x}\right]_n + wH_2O$$

where the numerical values of x, y, n and w are functions of the chemical preparation conditions and as such no stoichiometric hydrated zirconia are known to exist. At this stage the polymer containing the square planar tetramers appears to undergo elimination of physically bonded water trapped in the capillaries of partially dried gel-precipitates. The peak temperatures and the mass loss of the samples are very similar, with mass loss at this stage found to be about 23%wt, indicating that the chemical compositions of partially dried gels prepared with Zr^{4+}:H_2O initial molar ratios from 1:4.19 to 1:16.18 are very much alike. During the third stage of dehydration (375–450°C) of zirconia gels the remaining hydroxyls undergo condensation with the elimination of water according to the scheme proposed by Blesa *et al.* [8]:

$$\left[Zr_4O_{(8-x)}(OH)_{2x}\right]_n \rightarrow ZrO_{2(\mathrm{amorphious})} + H_2O$$

Increasing the initial Zr^{4+}:H_2O molar ratio decreases the DTG peak temperatures of elimination of unbounded hydroxo ligands, suggesting that this process is influenced by the water content in the starting reaction mixture.

Contrary, for the zirconium gels prepared from methanol solutions in which the initial Zr^{4+}:H_2O molar ratio did not exceed 1:4 value (Z1, Z2 and Z3 samples), three dehydration stages were also observed through the entire temperature range from 30 to 700°C. However, a marked difference is that the second DTG peak is less pronounced and dependent on the addition of water for hydrolysis. In this case the mass loss from devolatilization of the reaction medium and elimination of liquid water trapped in the gel pores is represented by a single, very broad dehydration process (30–400°C). The decrease in the peak temperature for the condensation of the remaining hydroxo ligands again implies that variations in the addition of water to the reaction mixture affect the zirconium gel surface properties, particularly the Zr–O bond characteristics. However, the exact affect of water deficit on the chemistry of gel formation (in particular on the co-ordination of zirconia sites in tetramer complexes during the olation process) has not been defined yet.

To deduce the exact reaction scheme for the thermal decomposition of zirconia gel-precipitates, an evolved gas analysis was included in the experimental program. The results of EGA are shown in Figs 2 and 3. As expected from the reactions mentioned above only water and methanol were detected during the thermal decomposition of hydrous zirconia. Although the gel-precipitates were separated from solution in which ammonium chloride was also present no ammonia or hydrochloric acid were detected by the used EGA analytical set-up. It was concluded that all mass losses during the thermal treatment of zirconia gel-precipitates are the consequence of the three different dehydration stages described above.

The kinetics of the stepwise dehydration processes of zirconia gels were analysed by subjecting the samples to TG, DTG studies at different heating rates. The peak temperatures (T_m) and the heating rates (Φ) are related through Kissinger's plot [6, 9] (Fig. 4).

$$\ln\left(\Phi(T_m)^{-2}\right) = \left(-E_a(RT_m)^{-1}\right) + k$$

The kinetic constant (k) and the activation energy (E_a) for the process were obtained from a plot of $\ln(\Phi(T_m)^{-2})$ *vs.* $(T_m)^{-1}$ and are revealed in Table 2. The activation en-

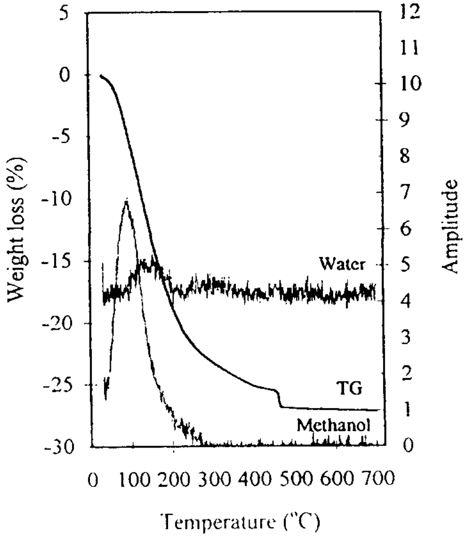

Fig. 2 Typical EGA pattern for Z1 sample

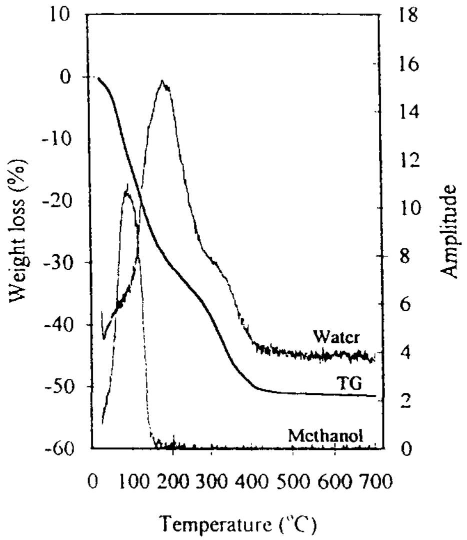

Fig. 3 Typical EGA pattern for Z4 sample

ergies and the kinetic constants values in the third dehydration step of zirconia gels are, with the alteration of the initial Zr^{4+}:H_2O molar ratio, substantially changed. If the theoretical amount of water needed for the complete hydrolysis of the zirconia precursor was added (Zr^{4+}:$H_2O > 1:4$, Z4-Z6 samples), the activation energy of condensation of remaining hydroxyls and elimination of water would be raised. Thus the kinetics of relaxation of the hydroxyl containing polymer is suppressed by

Table 2 Activation energies and kinetic constants of dehydration studies of various hydrated zirconia

Sample	Dehydration stage II.		Dehydration stage III.	
	E_a/kJ mol^{-1}	k/s^{-1}	E_a/kJ mol^{-1}	k/s^{-1}
Z1			309	$8.7 \cdot 10^{16}$
Z2			293	$1.5 \cdot 10^{16}$
Z3			280	$3.7 \cdot 10^{15}$
Z4	153	$1.7 \cdot 10^{11}$	461	$1.5 \cdot 10^{31}$
Z5	124	$7.9 \cdot 10^{7}$	453	$4.9 \cdot 10^{30}$
Z6	112	$5.1 \cdot 10^{6}$	451	$4.7 \cdot 10^{30}$

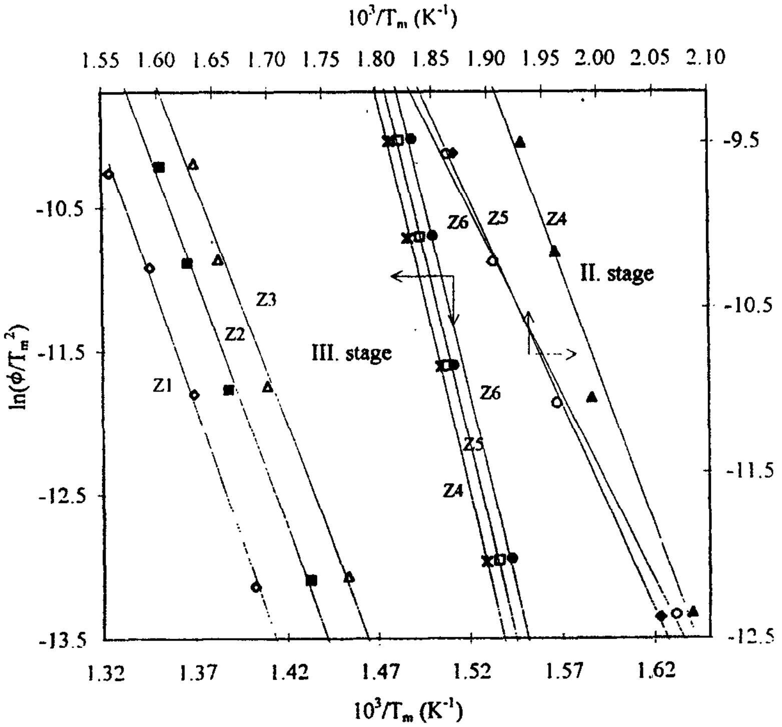

Fig. 4 Kissinger plots of zirconia gels prepared with different addition of water

the water content in the drying gel. We assumed, that the differences in the values of the kinetic parameters between the samples with excess or lack of water come from the different microstructual properties of these samples. In polar solvents such as alcohols, chloride-modified transformation metal alkoxides can be prepared by reaction of metal chlorides with alcohols (commercial process of metoxide preparation). Therefore, the greater reactivity of zirconium metoxide changes the subsequent hydrolysis reaction and requires that it should be processed with stricter control of moisture and conditions of hydrolysis in order to prepare gel-products rather than precipitates [10]. Modification of reaction conditions by controlled addition of water to the organic reaction medium enables a change of reaction mechanism. The addition of theoretical or excess amounts of water induces full hydrolysis of zirconium ionic species in the solution and formation of more defined particles. By lowering

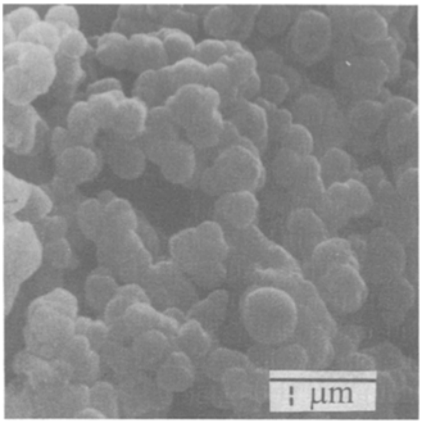

Fig. 5 SEM of Z1 sample before thermal treatment

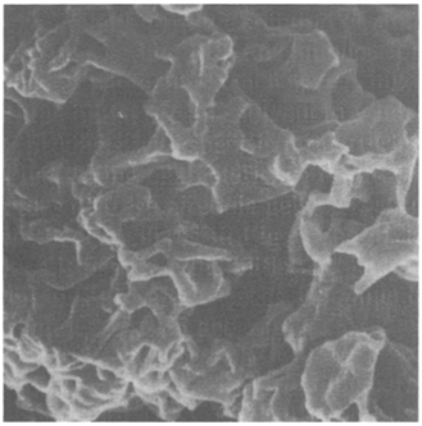

Fig. 6 SEM of Z6 sample before thermal treatment

the amount of water below the theoretically required ratio (Zr^{4+}:H_2O=1:4), a change in mechanism is observed. Due to the lack of water a metoxy group is included into the coordination sphere around zirconium and influences subsequent condensation reactions giving a product with opened gel structure. When the zirconia gels were prepared from the methanol solutions with the lack of water, the individual zirconia gel species are joined together into branched chains forming very porous gel structure (Fig. 5). On the other hand, spherical gel particles were observed when the zirconia gels were prepared from the water rich initial solutions (Fig. 6). The opened gel structure in comparison with the spherical particles gives smaller diffusion contribution in the activation barrier of the dehydration process.

Conclusions

During heat treatment of zirconia gel-precipitates prepared from methanol solutions three different stages of mass loss occur. The first stage of volatile loss is attributed to the evaporation of methanol and water from the surface of the gels. During the second stage, which occurs over a broad temperature range (155–375°C), the polymers undergo elimination of physically bonded water trapped in pores of partially dried gel. The relaxation of the remaining hydroxyls followed by the elimination of water takes place in the third stage of mass loss. This stage is strongly affected by the preparation conditions, especially by the initial Zr^{4+}:H_2O molar ratio. In the case of zirconia gels prepared from water deficient initial solutions the difference between the first and second stages of volatile loss is less pronounced. The microstructual properties of the products differ appreciably (spherical aggregated sol particles or formation of branched chains with a very porous and opened structure). The differences in microstructure between various products are reflected also in the values of the kinetic parameters. The activation energy and the kinetic constant are increased with an increase in the water content in the initial solution, and thus also with the shape of drying gels (diffusion contribution in the activation barrier).

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