Influence of Crystallite Size on the Properties of Zirconia

Wolfram Stichert and Ferdi Schüth*

Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität Frankfurt, Marie Curie Str. 11, 60439 Frankfurt am Main, Germany

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Systematic studies on the properties of zirconia for catalytic applications revealed that the concentration of the stock solution, from which precipitation is carried out, strongly influence the crystallite size of the resulting zirconia. The crystallite size influences the BET surface area, the crystallization temperature, and the phase transition temperature. The findings of this study clarify the parameters governing the formation of specific phase with desired surface areas.

Introduction

Zirconia has found a growing use in ceramics and catalysis. Especially its catalytical properties are promising since zirconia has both acid and basic properties,[1] as well as a high thermal stability. Therefore, many recent papers consider applications of zirconia as a catalyst or a catalyst support.[2−4] Factors influencing the specific surface area and the phase transformations of zirconia have therefore attracted great interest both in industry and universities. Special attention was given to the low-temperature phase transformations of zirconia, the crystallization, and the phase transformation between the metastable tetragonal and the monoclinic phases.

A common preparation route for zirconia consists first of a precipitation of hydrous zirconia with ammonia from a zirconium salt solution and, second, subsequent thermal treatment of the hydrous zirconia precipitate. This precipitate usually is amorphous; the crystallization occurs at about 450 °C, first to the metastable tetragonal phase. The transformation from the tetragonal to the monclinic phase takes place over a wide range of temperatures above 450 °C. The transformation temperature of a particular sample is very much depending on several chemical parameters, such as the pH after precipitation,[5] the precipitation kinetics,[6] and the presence of H_2O_2 during precipitation.[7] The presence of H_2O_2 does not only alter the temperature of the phase transformation but also lowers the temperature of crystallization. However, several reports have shown[8−11] that the phase transformation between the tetragonal and monoclinic phases occurs not on heating but on cooling. This led to the conclusion[11] that a particular crystallite has a transformation temperature for the phase transformation during cooling which can be above room temperature (the transformation takes place) or below room temperature (the crystallite stays tetragonal). The transformation is accomplished more readily in an air or oxygen atmosphere than in an inert gas atmosphere.[12] The presence of anions influences also both the temperature of the transformations and the specific surface area. Especially, the influence of the sulfate anion was extensively studied.[7,12−14] The presence of sulfate stabilizes the tetragonal phase and increases the surface area, whereas carbonate tends to lower the surface area.[14] Ethanol washing of the hydrous precursor increases the specific surface area and promotes the tetragonal to monoclinic phase transformation of zirconia.[15] Another factor facilitating the phase transformation from tetragonal to monoclinic is water vapor.[16,17] Clearfield succeeded in crystallizing the hydrous zirconia precursor by boiling it in water.[18−20] Depending on the pH conditions, he got either a monoclinic or a tetragonal product. We made similar observations after aging the precipitate in mother liquor or treating it under mild hydrothermal conditions.[21] It is

* To whom correspondence should be addressed. Tel.: 069/798 29252. Fax: 069/798 29260. E-mail: ferdi@schueth.chemie.uni-frankfurt.de.

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also possible to cause a phase transformation by milling.[17,22]

Possible explanations for the factors determining the low-temperature phases of zirconia have been controversely discussed. Garvie[23,24] was the first to propose that the sum of the free energy from surface, bulk, and strain effects determines the stability of a single crystallite of zirconia. Because of the lower bulk free energy of the monoclinic phase and the lower surface free energy of the tetragonal phase, the tetragonal phase is stabilized below a critical particle size. Below this particular particle size, the surface term should dominate the bulk term. According to Garvie, this particle size is 300 Å. Cationic dopants in the bulk of zirconia also stabilize the tetragonal phase, which can be explained by a bulk free energy effect. However, it was proven that this effect at least is not the only one being responsible for the phase transformation.[25] Another explanation considers domain boundaries being responsible for the stabilization of the tetragonal phase due to the strain caused by the transformation of a particle being surrounded by untransformed particles.[26] However, there is general agreement that this transformation is martensitic,[27,28] so the strain effect should be small. Many papers report the presence of a nucleation site being a prerequisite for the phase transformation.[29-32] This argument could also account for a crystallite size effect, since in smaller cystallites there is a smaller probability for the presence of a nucleation embryo of a critical size.[32]

Short-range structural similarities of the amorphous precursor and the tetragonal phase are thought to account for the occurrence of the low-temperature tetragonal phase.[33] Since a microcrystallinity with a grain size of 15-30 Å was reported for hydrous zirconia,[34] the crystallization would then be an agglomeration of small crystallites to larger crystallites detectable by XRD. Other reports state that the initial nucleation of tetragonal zirconia is favored by creation of anionic vacancies with trapped electrons.[35,36]

Not only the crystal phase but also the specific surface area of zirconia is influenced by several factors. The drying conditions of the hydrous zirconia are reported to be of importance,[14] as well as a digestion of the gel at 80 °C.[37] Lin and Duh reported an influence of the concentration of the stock solution on the specific surface area and the crystallite size[38] in the range between 0.25 and 1 M in the system $CeO_2-Y_2O_3-ZrO_2$.

Like many other hydrous metal oxides, zirconia undergoes a strong exothermic transition, known as the "glow phenomenon". This phenomenon, easily observable in a DTA measurement, is generally attributed to the crystallization of zirconia.[39] However, at least for hafnium–zirconium mixed oxides and for hafnia, the crystallization and the glow phenemenon are different events.[40] The magnitude of the glow phenomenon decreases as the atmosphere is changed from static air through nitrogen to hydrogen.[39] The temperature of the occurrence of the DTA peak can be altered by means of the addition of water to the gel,[39] by adding H_2O_2 to the precipitation solution,[7] or by adding anions.[14]

In our systematic studies on the properties of zirconia for catalytic applications, we found that the concentration of the stock solution from which precipitation is carried out dramatically influences the properties of the resulting zirconias. This gives new insight in the parameters governing these properties. In addition, it led to the discovery of a process to prepare zirconias which retain high surface areas even after heat treatment at 950 °C for 5 h.

Experimental Section

The zirconia samples were prepared in the following way: A stock solution of $ZrOCl_2\cdot8H_2O$ (ABCR, 95%) was prepared. The concentration of the zirconium salt was varied in the range between 0.0025 and 0.1 M. After stirring for five minutes, an aqueous solution of NH_4OH (Roth, 25%) was added in excess to a pH of 10 ± 0.2. The resulting precipitate was filtered off, washed with deionized water, and dried at 90 °C for 24 h. Subsequently, the hydrous oxide was calcined for 5 h at different temperatures, always heating with a rate of 1 K/min to the desired temperature.

The X-ray diffraction (XRD) patterns were recorded using a Stoe STADI P diffractometer equipped with a germanium monochromator in transmission geometry. The scans were taken within the range of 27° to 34.5° (2θ) using Cu Kα radiation. The volume fraction of the monoclinic phase (V_m) was determined by the empirical formula

$$V_m = 1.311X_m/(1 + 0.311X_m)$$

[41] where the integrated intensity ratio was

$$X_m = [I_m(111) + I_m(11\bar{1})]/[I_m(111) + I_m(11\bar{1}) + I_t(111)]$$

with I_m being the intensities of the monoclinic peaks and I_t the intensities of the tetragonal peaks.

The crystallite sizes were calculated by means of a procedure contained in the Stoe Visual X^{POW} software package, the single line size/strain Fourier analysis. Due to the fact that only one peak with relatively low intensity could be analyzed, these values are fairly uncertain. The trends, however, are calculated correctly.

The nitrogen adsorption–desorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 system. Prior

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Table 1. Volume Fraction of the Monoclinic Phase of all the Samples

concn, M	volume fraction (%)									
	350 °C	400 °C	450 °C	550 °C	650 °C	750 °C	850 °C	950 °C	1050 °C	1150 °C
0.0025	amor.	amor.	amor.	amor.	amor.	0	0	0	0	100
0.004	amor.	amor.	amor.	amor.	0	0	0	0	0	100
0.01	amor.	amor.	amor.	0	0	0	0	0	33	100
0.02	amor.	0	0	0	0	0	0	27	84	100
0.03	amor.	0	0	0	0	65	60	74	89	100
0.06	0	0	0	66	79	84	85	88	91	100
0.1	0	0	0	81	85	90	92	90	91	100

Table 2. Crystallite Sizes of All Samples[a]

concn, M	350 °C	400 °C	450 °C	550 °C	650 °C	750 °C	850 °C	950 °C	1050 °C	1150 °C
0.0025	amor.	amor.	amor.	amor.	amor.	t10 nm	t9.1 nm	t9.6 nm	t18.4 nm	m15.3 nm
0.004	amor.	amor.	amor.	amor.	t11.5 nm	t11.5 nm	t11.4 nm	t10.9 nm	t19.2 nm	m19.1 nm
0.01	amor.	amor.	amor.	t11 nm	t11.1 nm	t12.7 nm	t13.8 nm	t15.5 nm	t26.7 nm	m20.8 nm
0.02	amor.	t11.8 nm	t15 nm	t13.3 mn	t15.1 nm	t15.2 nm	t16.2 nm	t17.4 nm	m14.3 nm	m23.7 nm
0.03	amor.	t15.5 nm	t16.5 nm	t16.4 nm	t16.7 nm	t17.5 nm	t16.2 nm m15.1 nm	t18.0 nm m13.3 nm	m17.4 nm	m26.3 nm
0.06	t16 nm	t15.3 nm	t16.5 nm	t20.6 nm m10.7 nm		m12.8 nm	m16.3 nm	m16.2 nm	m15 nm	m20.8 nm
0.1	t15.8 nm	t14 nm	t15 nm	m10.3 nm	m14.5 nm	m18.9 nm	m21.1 nm	m21.2 nm	m25.7 nm	m34.8 nm

[a] The index "m" means a crystallite size of a monoclinic crystallite, "t" means a tetragonal crystallite.

to the measurements, the samples were outgassed for 4 h at 120 °C. The specific surface areas of all samples were calculated according to the BET method.[42] The pore size distribution was calculated according to the BJH method.[43] This method was applied to the adsorption isotherm, because the shape of the hysteresis loops suggests the presence of a network percolation effect.[44] The BJH adsorption average pore diameter was calculated by means of the BJH adsorption cumulative surface area and the BJH adsorption cumulative pore volume of pores between 17 and 3000 Å with the formula $4V/A$, assuming a cylindrical pore geometry.

The thermogravimetric (TG) and differential thermal analysis (DTA) measurements were carried out using a Setaram TG-DTA 92-16. The samples were heated continuously with a rate of 10 K/min from 288 to 1273 K in a static air atmosphere.

Results

Eight different hydrous zirconia samples were prepared under identical conditions, i.e., a pH of 10 ± 0.2 after precipitation and a drying time of 24 h at 90 °C in a static air atmosphere. Only the concentration of the $ZrOCl_2 \cdot 8H_2O$ solution was varied in the range between 0.0025 and 0.1 M, indicated in the following text by Zr-(0.0025), etc. These hydrous zirconia samples were calcined always for 5 h and with a heating rate of 1 K/min at different temperatures in the range between 350 and 1150 °C. The result was a set of 70 zirconia samples. An XRD of each sample was measured, and the crystallite size and the monoclinic volume fraction were calculated. A nitrogen adsorption isotherm of the samples calcined at 550 and 950 °C was measured and a DTA measurement of some hydrous zirconia samples was performed. To check the reproducibility of the preparation, several of the samples were prepared twice or more often. Deviations of the properties were always found to be within 10%.

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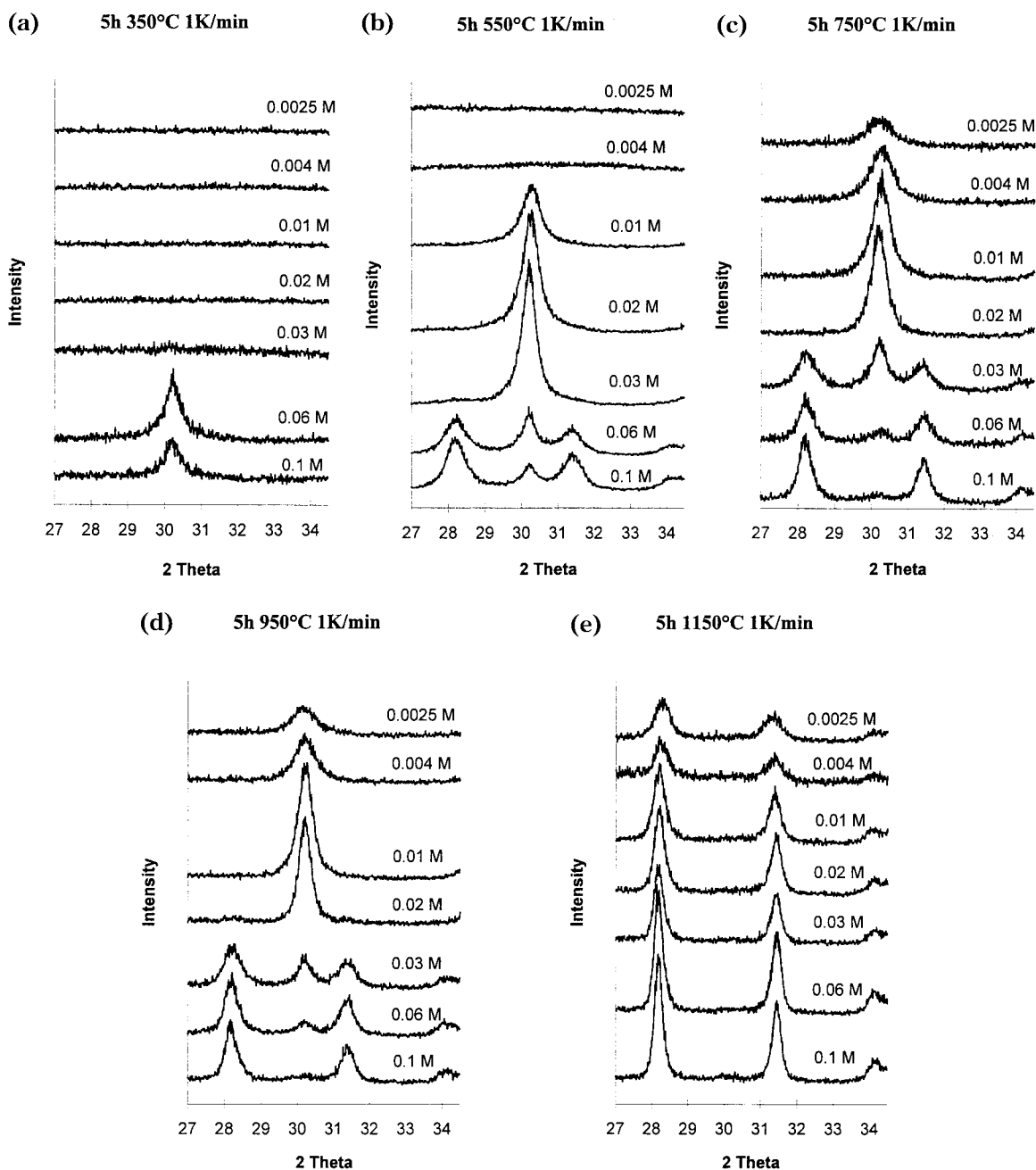
Figure 1a–e shows the X-ray diffractograms of the zirconia samples calcined at different temperatures. Most of the samples calcined at 350 °C are amorphous. Only the samples prepared at higher concentrations show the tetragonal phase. The samples calcined at 550 °C are mainly monoclinic for the highest concentrations. The more dilute the concentrations are, the smaller is the monoclinic volume fraction, as can be seen in Table 1 in more detail. Zr(0.03) is purely tetragonal. Zr-(0.0025) and Zr(0.004) are still amorphous, which is quite surprising. Table 2 shows the approximate crystallite sizes of the phase which has the higher volume fraction in the sample. The more dilute the stock solutions are, the smaller are the crystallites of one particular phase. However, the monoclinic crystallites are generally smaller than the tetragonal ones, as reported in recent studies.[12] The diffractograms of the samples calcined at 650 °C show a larger monoclinic fraction at higher concentrations and generally a larger crystallite size. Zr(0.004) is now tetragonal, not amorphous any more. At 750 °C, Zr(0.0025) is crystalline as well, and Zr(0.03) exhibits now a detectable monoclinic fraction. Between 750 and 950 °C the crystallite sizes of all samples do not grow significantly, and the phase composition does not alter very much. At 1050 °C, most samples show a different diffractogram than at 950 °C. The phase composition is strongly shifted toward the monoclinic phase, and the crystallite sizes are much larger than at 950 °C. However, it should be noted that the samples precipitated from very dilute Zr solutions are still tetragonal. At 1150 °C all samples are monoclinic. However, the crystallite sizes are still different, depending on the concentration of the stock solution.

A DTA measurement was performed to check the possible influence of the Zr concentration at precipitation on the crystallization temperature. The diffractograms of the samples calcined at 550 °C suggest such a connection. The strong exotherm appearing in DTA graphs of zirconia is due to the crystallization, as pointed out in the Introduction. Figure 2 shows the DTA curves of five of the hydrous zirconia samples. At

(a)　　**5h 350°C 1K/min**　　　　**(b)**　　**5h 550°C 1K/min**　　　　**(c)**　　**5h 750°C 1K/min**

(d)　　**5h 950°C 1K/min**　　　　　　**(e)**　　**5h 1150°C 1K/min**


Figure 1. Diffractograms of zirconia samples calcined for 5 h at 350 °C (a), 550 °C (b), 750 °C (c), 950 °C (d), and 1150 °C (e) at heating rate of 1 K/min obtained from stock solutions with different zirconium concentrations: 2.5 mM to 0.1 M.

very dilute concentrations, there is obviously an influence of the Zr concentration on the crystallization temperature. It is not a contradiction that the glow peak of Zr(0.0025) appears at about 800 °C, whereas the diffractogram at 750 °C of this sample shows an at least partly crystallized structure, because the total time the zirconia sample is exposed to a particular temperature is important as well. The DTA measurements were performed with a heating rate of 10 K/min, consequently the absolute temperatures cannot be compared directly with the XRD results which are obtained after calcination for 5 h.
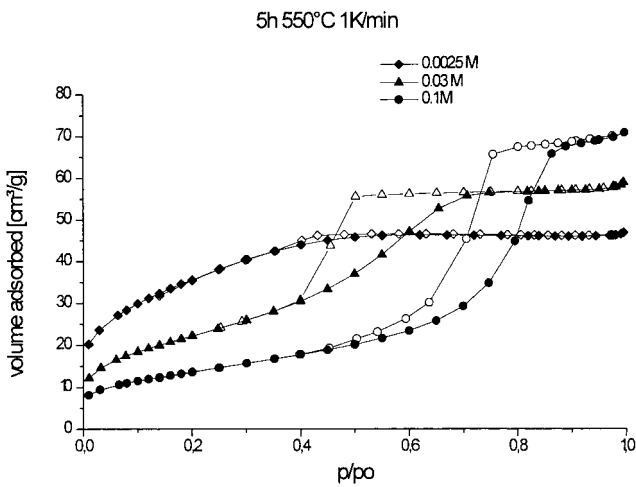
Figure 3 shows the nitrogen adsorption isotherms of selected samples calcined at 550 °C, and Figure 4 shows the BET surface areas of the samples calcined at 550 and 950 °C extracted from the isotherm. As can clearly be seen, the specific surface area increases with de-

creasing concentration. The surface areas are clearly correlated with the size of the zirconia particles. Zr-(0.0025) and Zr(0.004) are not crystalline at 550 °C; these samples show a partial microporosity. Since microporosity can result in the calculation of misleading BET surface areas,[45] one has to be careful in interpreting the BET surface areas of these two samples. The BET surface area is not the only parameter connected with the size of the particles. The larger the particles are, the more the pore size distribution should be shifted toward larger pore sizes and consequently the average pore diameter should be bigger. Figure 5 shows the BJH adsorption average pore diameter of all samples calcined at 550 °C and 950 °C. Figure 6 shows the
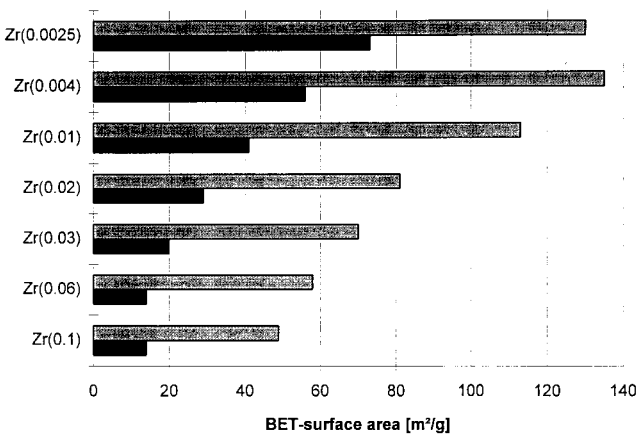
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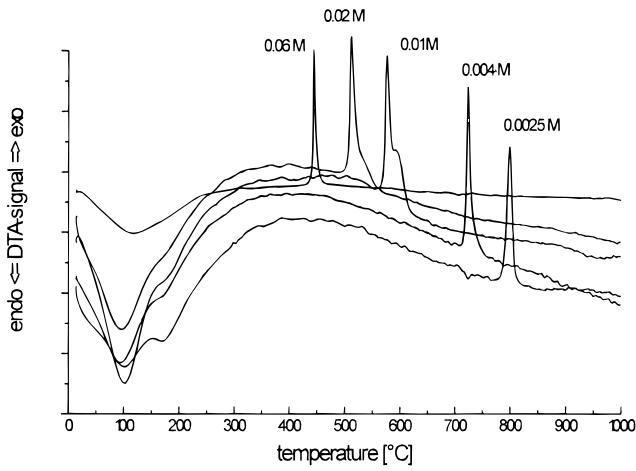
Figure 2. DTA experiments with hydrous zirconia samples precipitated from different zirconium concentrations: 2.5 mM to 0.1 M.
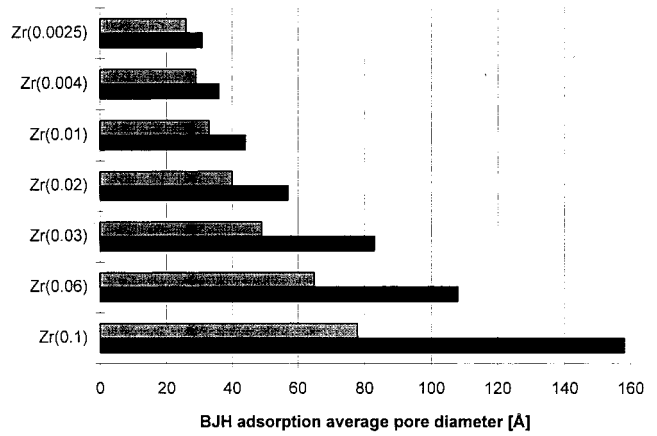

Figure 3. Nitrogen adsoption isotherms of zirconia samples calcined for 5 h at 550 °C with a heating rate of 1 K/min.


Figure 4. BET surface areas of the samples calcined at 550 (upper bar) and 950 °C (lower bar).
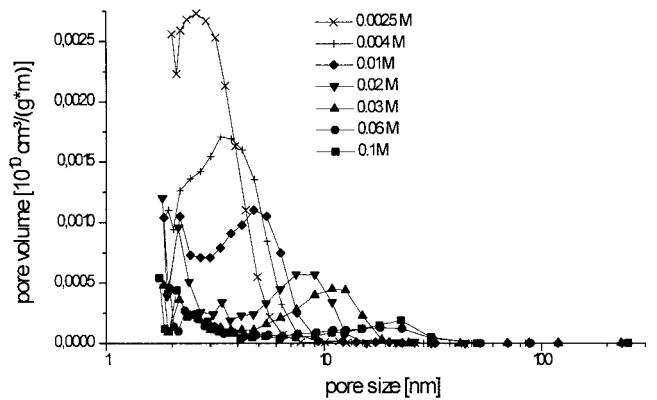
adsorption pore size distribution of the samples calcined at 550 °C, and Figure 7 shows the adsorption pore size distribution of the samples calcined at 950 °C. It can clearly be seen that for both calcination temperatures the average pore diameter decreases and the pore size distribution is shifted to lower values with lower concentrations of the stock solutions. The BJH method, however, is only valid for mesopores. Pores smaller

Figure 5. BJH adsoption average pore diameters of the samples calcined at 550 (upper bar) and 950 °C (lower bar).
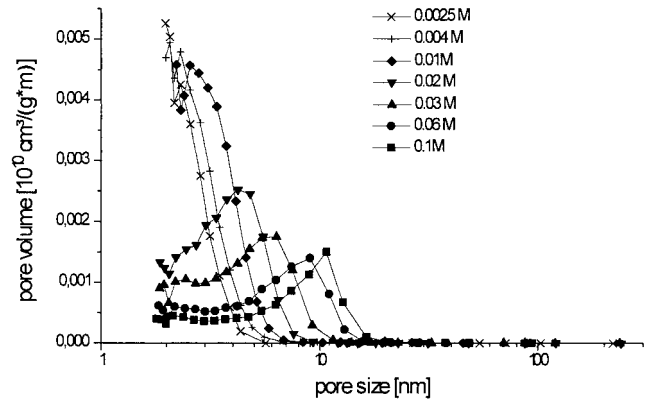
Figure 6. BJH pore size distribution of the samples calcined for 5 h at 550 °C with a heating rate of 1 K/min.

Figure 7. BJH pore size distribution of the samples calcined for 5 h at 950 °C with a heating rate of 1 K/min.

than 17 Å in diameter are therefore not included in the calculation of the average pore diameter. The samples prepared from stock solutions with a low Zr concentration which are calcined at 550 °C most probably contain pores below 17 Å in diameter. The validity of the BJH average pore diameter value of these samples is therefore limited.

A part of Zr(0.0025) was dried according to the method of Norman et al.[14] in the presence of water vapor to increase the specific surface area and calcined for 5 h at 950 °C with a heating rate of 1 K/min. This sample exhibits a specific surface area of 109 m²/g, which, as far as we know, is the highest reported surface area for zirconia calcined under such severe conditions.

Influence of Crystallite Size on Zirconia

Chem. Mater., Vol. 10, No. 7, 1998 2025

Table 3. Particle Sizes of the Samples Calcined at 550 and 950 °C Derived from the BET Surface Area Assuming a Spherical Particle Shape

concn, M	550 °C	950 °C
0.0025		13 nm
0.004		18 nm
0.01	9 nm	24 nm
0.02	12 nm	34 nm
0.03	14 nm	52 nm
0.06	18 nm	74 nm
0.1	21 nm	74 nm

Table 3 shows the particle diameters of the samples calcined at 550 and 950 °C derived from the BET surface area assuming a spherical shape of the particles. The size of the amorphous particles was not calculated because of the limitations of the BET theory when the sample contains micropores. Zr(0.01), Zr(0.02), and Zr-(0.03), calcined at 550 °C, show about the same particle sizes as crystallite sizes calculated from the XRD line broadening. The lower the concentration is, the smaller is the difference between BET and XRD particle size for samples calcined at 950 °C. Crystallites of samples prepared at higher concentrations seem to agglomerate more readily than crystallites of samples prepared at lower concentrations.

Discussion

The essential results of the study are the following: varying the concentration of the stock solution leads, after calcination, to different crystallite sizes, different particle sizes, and different phase compositions of the samples. At very low concentrations, a surface area of the zirconia samples of above 100 m²/g can be achieved after calcination at 950 °C. The first conclusion derived from the differences in crystallite and particle sizes is that a more dilute concentration of the stock solution will lead to the precipitation of smaller precursor primary particles, which grow during calcination to smaller crystallites and particles, respectively. This is somewhat unexpected, since at low concentrations usually a lower supersaturation should lead to the formation of bigger particles. However, the nature of solution species (oligomer distribution) will be dependent on the concentrations, which could influence particle sizes as well. The temperature of the phase transformation and the crystallization of a particular sample are also dependent on the concentration of the stock solution and consequently most probabely dependent on the precursor primary particle size.

These dependencies can be explained by Scheme 1, which will serve an the basis for the discussion. As stated above, an influence of the crystallite size on the phase transformation temperature was reported before. Our results add further confirmation to the importance of the crystallite size for the tetragonal to monoclinic phase transformation of zirconia. However, since there are two different explanations for this effect, a further disussion is necessary. It must be discussed whether this is an effect caused by different bulk and surface free energies of tetragonal and monoclinic zirconia, as proposed by Garvie, or an effect of embryonic nuclei, which transform a domain when they reach a critical size. These nuclei are indirecly connected to the crystallite size, because the probability that a crystallite

Scheme 1. Influence of the Precursor Particle Size on the Phase of Zirconia
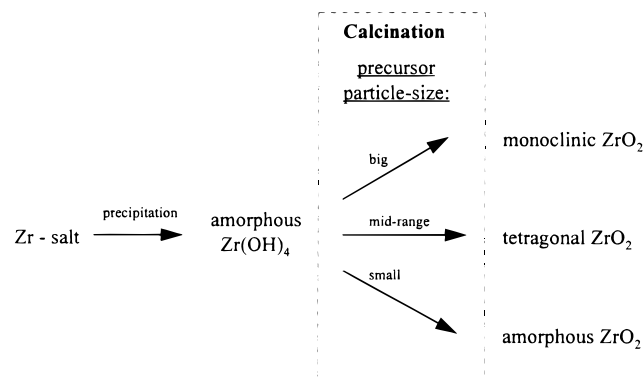
contains an embryo of the critical size is related to the crystallite size itself.

The hypothesis that embryonic nuclei of a particular critical size are responsible for this phase transformation seems to be more probable, because our data show that monoclinic crystallites can be smaller than tetragonal ones. If it were true that tetragonal crystallites transform to monoclinic crystallites because monoclinic crystals above a critical crystallite size are energetically preferred, it would be difficult to understand why the monoclinic crystals after the phase transition should be smaller than the former tetragonal ones. However, if the embryonic nuclei were responsible for the nature of the resulting phase, the particle size would be only one factor among others.

A second transformation, which is obviously influenced by the concentration of the stock solution, is the crystallization. The crystallization is thought to be an agglomeration of small crystal precursors having a structure similar to the tetragonal phase. This agglomeration seems to need a critical size of the agglomerating precursors. The size of these precursors is dependent on the concentration of the stock solution and the calcination conditions.

In light of these findings, previous literature data can be reinterpreted to give a more consistent picture of the crystallization of zirconia.

1. Influence of H₂O₂. In our case an embyonic nuclei effect seems to be responsible for the phase transformation, but it is clear that this cannot be the only effect influencing the temperature of phase transformation. Navio et al.[7] report the influence of H_2O_2. This parameter seems to have at least three effects: a lower crystallization temperature, a lower BET surface area, and a tetragonal to monoclinic phase transformation shifted to higher temperatures. In light of our data, these results can be interpreted as a combination of two overlapping effects: an increase in particle size, which could explain the lower specific surface area and the occurrence of the DTA peak at lower temperatures, and the chemical effect reported by the authors, which must be the more important one with respect to the phase transformation in the light of their results. This chemical effect probably is a particle surface effect, which then also could explain the observation that calcination in an inert gas atmosphere also alters the phase transformation temperature.[10] The influence of the pH at precipitation on the phase of zirconia could be due to this effect as well.

2. Influence of Sulfate. The well-known effect of sulfate groups increasing the surface area of zirconia and the occurrence of almost only the tetragonal phase in sulfated zirconia can also be interpreted as a crystallite size effect. As Navio et al. report,[7] the surface area of uncalcined sulfated hydrous zirconia is as large as the surface area of the corresponding nonsulfated hydrous zirconia samples. The role of the sulfate groups could therefore be an inhibition of the agglomeration of the primary crystallites. The crystallite size stays small, the phase transformation is inhibited, the specific surface area stays high, and the crystallization temperature is shifted to higher temperatures. However, there is still a possibility that sulfate groups also have a chemical particle surface effect similar to that of H_2O_2.

3. "Scaffolding Mechanism". The crystallite size effect could also account for results which were reported for the system zirconia−alkyltrimethylammonium halides.[46,47] The authors report surface areas of over 200 m^2/g for samples mainly calcined at 500 °C. An XRD of a sample calcined at 600 °C shows that this sample is almost amorphous. It is well-known that amorphous zirconia can have a high surface area in the range

reported by the authors, which is due to the presence of small particles. These could be induced by the presence of the surfactant. This explanation seems to be more straightforward than the "scaffolding mechanism" proposed by the authors. The surfactant could also have the effect of inhibiting crystallite agglomeration during calcination. This would, however, lead to the same results, i.e., small particles and the corresponding high surface areas.

Conclusion

The following are the main findings of this study: (1) Zirconia calcined at 950 °C for 5 h with a surface area of over 100 m^2/g could be prepared. (2) It is possible to adjust the phase and the crystallization temperature with the zirconium salt concentration during precipitation. (3) It is possible to adjust the specific surface area of zirconia even at elevated temperatures with the zirconium salt concentration. (4) The alteration of the phase transformation and the crystallization temperature can be interpreted in this case as a crystallite size effect. (5) Some other effects, such as the influence of the sulfate groups, surfactant, or H_2O_2, could be interpreted as effects connected with the crystallite size of zirconia.

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