The Influence of pH on Zirconia Formed from Zirconium(IV) Acetate Solution: Characterization by X-Ray Powder Diffraction and Raman Spectroscopy

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The influence of the pH of the reaction mixture on the nature of zirconia formed from zirconium(IV) acetate solutions, processed either by boiling under reflux or by hydrothermal methods, has been investigated. The resulting gels and powders were calcined in air at various temperatures and characterized using X-ray powder diffraction and Raman spectroscopy. The latter technique was found to be superior in differentiating between tetragonal and cubic zirconia. Zirconia formed from solutions of high pH was found to contain a greater quantity of the tetragonal polymorph, suggesting that the addition of alkali to the solution tends to stabilize the tetragonal form against conversion to the monoclinic form. The high pressure associated with the hydrothermal treatment is important for the direct formation of monoclinic zirconia under acidic conditions. © 1999 **Academic Press**

INTRODUCTION

Pure zirconium dioxide can be crystallized with a cubic, tetragonal, monoclinic, or, at elevated pressures, orthorhombic structure. The cubic polymorph adopts the calcium difluoride (fluorite) structure in which the zirconium atoms are coordinated to eight oxygen atoms, while the tetragonal phase may be regarded as a slightly distorted fluorite structure whose diffraction patterns can be indexed to a face-centered tetragonal cell. The monoclinic polymorph, which is sometimes referred to as the Baddeleyite structure, contains zirconium atoms seven-coordinated to oxygen atoms (1).

The monoclinic form of zirconium dioxide is usually found at room temperature. It undergoes a reversible martensitic (2) phase transformation at 1174°C to a high temperature tetragonal phase (3), which cannot be retained by quenching and which reverts to the monoclinic structure at 900°C (4). It has also been suggested (5) that the monoclinic to tetragonal transformation is dependent on the particle size, with a critical size of ~10 nm. The tetragonal phase remains unaltered by further thermal treatment until the temperature reaches 2370°C, whereupon it transforms into the cubic phase, which is stable up to the melting point at 2680°C (6).

A tetragonal phase, which is reported to be identical to the high-temperature one (7), can be formed at room temperature by adding aqueous ammonia to a zirconium(IV) oxychloride solution and heating the resulting gel, described as zirconium hydroxide, at 110°C and subsequently at 500°C. Other workers (8,9) have found that the low temperature tetragonal phase of zirconium dioxide can be formed by heating zirconium(IV) hydroxide gel at 290 or 350°C. This tetragonal phase is reportedly converted at temperatures between 350 and 600°C to the monoclinic polymorph (8).

In recent years there has been an increasing interest in the preparation of ultrafine zirconia powders (10–15) because of the widespread, well-documented use of stabilized zirconia ceramics for both structural and functional applications, as well as the development of zirconia-toughened ceramics (16,17) and zirconia fiber coatings for oxide–oxide ceramic matrix composites (18–20). Particular emphasis has been placed upon hydrothermal processing, sol-gel, and precipitation routes for the synthesis of products with well-defined particle size, morphology, and crystal polymorph. It seems that the pH of the reaction mixture is a variable which has a considerable influence on the nature of the zirconia obtained. However, discrimination between the cubic and tetragonal phases by X-ray powder diffraction has proved to be difficult. The study reported here is an investigation of the influence of pH on the nature of the zirconia which can be formed from zirconium(IV) acetate solution, either by boiling under reflux or by hydrothermal processing. Raman spectroscopy was used in this work to distinguish between cubic and tetragonal zirconia.

EXPERIMENTAL

Solid zirconium(IV) acetate (MEL Chemicals) was dissolved in water to produce a $0.12 \, \text{mol dm}^{-3}$ solution, the pH of which could be adjusted by addition of hydrochloric acid or aqueous ammonia. The solutions were either boiled under reflux for 2.5 h or heated in a Teflon-lined autoclave at 220°C under autogenous pressure (ca. 10 bar) for 2.5 h. The cooled solutions were evaporated to dryness under an infrared lamp and the products calcined in air at 200, 500, 900, and 1400°C for 3 h.

X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer using CuK_α radiation. Raman spectra were taken using a Dilor XY spectrometer, with excitation at 514.5 nm provided by a Coherent 170 Ar^+ laser. Radiation power at the sample was varied between 5 and 15 mW. Infrared spectra were recorded with a Nicolet 205 FTIR spectrometer.

RESULTS AND DISCUSSION

The percentage of monoclinic zirconia produced was quantified from the X-ray powder diffraction patterns according to methods which have been described previously (21). The unequivocal identification of tetragonal or cubic zirconia by X-ray powder diffraction (22,23) recorded from the calcined materials was, as noted by other workers (24), precluded by peak broadening arising from poor crystallinity or small particle size. Tetragonal and cubic phases both produce a broad diffraction peak at $2\theta = 30°$ (Fig. 1), making differentiation between the two difficult.

In cases where the presence of a non-monoclinic crystalline phase of zirconia was indicated by the X-ray powder diffraction pattern, Raman spectroscopy was employed to identify the phase(s) present. The contrast between the Raman spectra obtained for different phases is evident in Fig. 2; by comparison with earlier experimental work, these spectra are assigned to the cubic (25) and tetragonal (26) phases, respectively.

The nature of the zirconia obtained under the various experimental conditions investigated in this study is summarized in Tables 1 and 2.

Zirconia Prepared by Boiling a Solution of Zirconium(IV) Acetate under Reflux

Discussion of the aqueous chemistry of zirconium has been generally confined to studies of oxozirconium(IV) halides, primarily oxozirconium(IV) chloride (27–35). From these studies it has been established that the major Zr(IV) species present in solution is a tetramer, probably the ion $[Zr(OH)_2 \cdot 4H_2O]_4^{8+}$ as established by X-ray crystallography in $ZrOCl_2 \cdot 8H_2O$ but possibly a related species carrying only a 4+ charge (35–37). It is envisaged that boiling an aqueous solution of zirconium (IV) acetate under reflux causes a slow polymerization of the aqueous zirconium species into $[Zr(OH)_4]_n$, which has a two-dimensional structure (38). The results recorded here suggest that drying
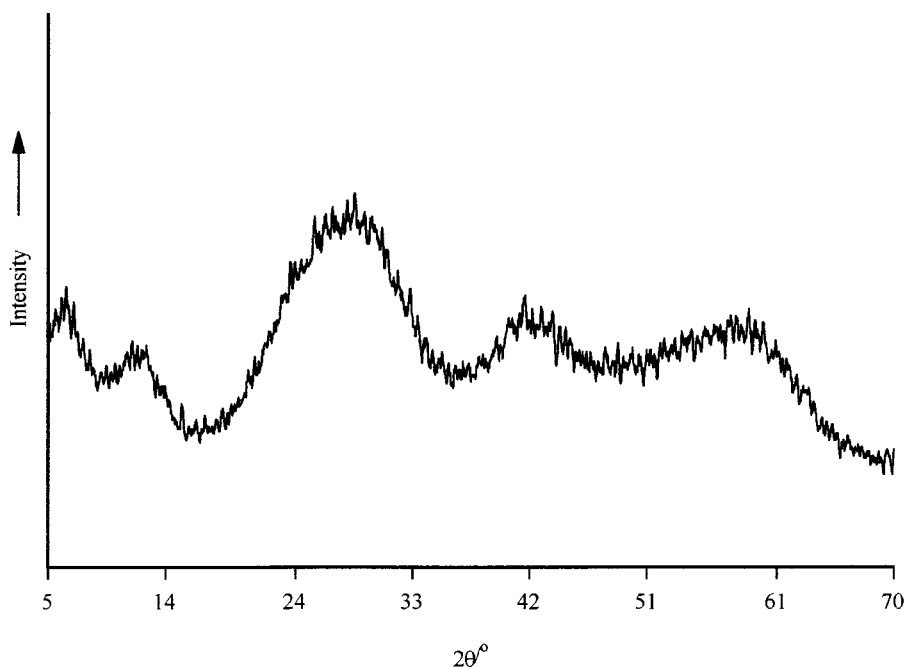

FIG. 1. X-ray powder diffraction pattern recorded from the reaction product which was produced by boiling an aqueous solution of zirconium(IV) acetate under reflux followed by drying under an infrared lamp.
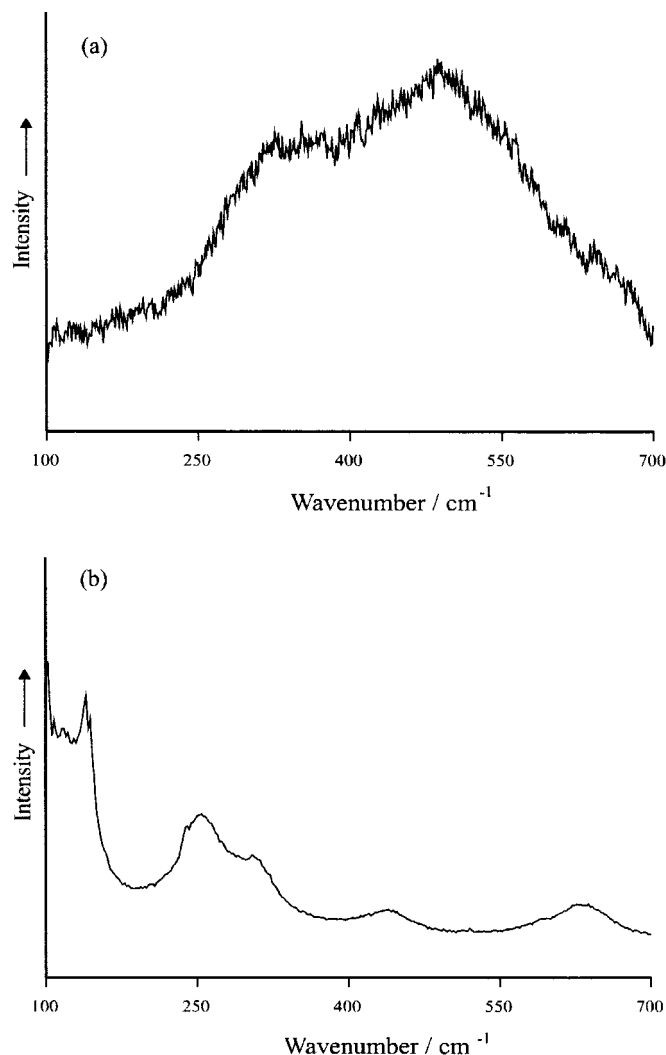
FIG. 2. Raman spectra of the reaction products which were produced by boiling an aqueous solution of zirconium(IV) acetate under reflux followed by drying under an infrared lamp and calcining in air at (a) 200°C (cubic), (b) 500°C (tetragonal).

under an infrared lamp dehydrates the polymeric zirconium(IV) hydroxide to a poorly crystalline form of cubic zirconia. The crystallinity of this cubic phase increased when the sample was heated to 200°C, the phase transforming to the fluorite-related tetragonal form at 500°C. Partial transformation to the monoclinic form was observed at 900°C, the transformation being complete at 1400°C.

The addition of ammonium hydroxide to zirconium(IV) acetate solution is likely to give a precipitate of hydrous zirconia by hydrolytic polymerization (27,38). On heating at 500°C this precipitate appears to undergo a thermally induced condensation to tetragonal zirconia. The small amount of monoclinic zirconia (ca. 3%) which was identified when the precipitate was heated to 900°C is indicative of the influence of ammonia in providing OH^- groups in the amorphous material, which has been found to stabilize the tetragonal polymorph (24,39). The stabilization of the tetragonal polymorph has been investigated in some detail (40) for materials produced by precipitation from zirconium sulfate solutions, the tetragonal-monoclinic transformation temperature being influenced by the high pH of the reaction mixture. Further, investigation (38) of the ZrO_2 phase formed from oxozirconium(IV) chloride solutions boiled under reflux at high pH also indicated stabilization of the tetragonal polymorph. These observations are in general agreement with the results reported here for zirconia prepared from zirconium(IV) acetate solutions by boiling under reflux.

The production of the hydrated form of oxozirconium(IV) chloride, $ZrOCl_2 \cdot xH_2O$, from a solution containing hydrochloric acid presumably reflects the reaction of aqueous $[Zr(OH)_2 \cdot 4H_2O]_4^{8+}$ with chloride ions (41). The crystallinity of the oxozirconium(IV) chloride is found to be dependent upon the pH of the solution being boiled under reflux, with solutions of lower pH leading to less crystalline samples. It is possible that the structure of the oxozirconium(IV) chloride is closely related to that of

TABLE 1

Results of X-ray, Raman, and Infrared Spectroscopic Analyses on the Nature of the Zirconia Formed by Boiling under Reflux Aqueous Solutions of Zirconium(IV) Acetate under Various Experimental Conditions

		Product of processing procedure					
			Calcined in air at various temperatures				
Preparative method	Dried under IR lamp		200°C		500°C		900°C	1400°C
Reflux/H₂O	Cubic[r]	0[m]	Cubic[r]	0[m]	Tet.[r]	0[m]	87[m]	100[m]
Reflux/NH₄OH pH 10	XRA[a]	0[m]	XRA[a]	0[m]	Tet.[r]	0[m]	3[m]	100[m]
Reflux/HCl pH 1[1]	$ZrOCl_2 \cdot xH_2O^{x,ir}$	0[m]	XRA[b]	0[m]	Tet.[r]	0[m]	77[m]	100[m]
pH 0.5	$ZrOCl_2 \cdot xH_2O^{x,ir}$	0[m]	XRA[b]	0[m]	Tet.[r]	0[m]	57[m]	100[m]

Notes. 1, See Fig. 3; cubic, cubic zirconia; tet., tetragonal zirconia; *r*, phase determined by Raman spectroscopy; *x, ir*, determined by X-ray powder diffraction and infrared spectroscopy; *m*, percentage of monoclinic zirconia present in sample (accuracy $+/- 3$ mol%) by method of Ref. (21); XRA, uncharacterized material which is amorphous to X rays; [a]suspected hydrous zirconia; [b]suspected chloride-containing hydrous zirconia.

TABLE 2
Results of X-ray, Raman, and Infrared Spectroscopic Analyses on the Nature of the Zirconia Formed by Hydrothermal Processing of Aqueous Solutions of Zirconium(IV) Acetate under Experimental Conditions

|	Product of processing procedure				
		Calcined in air at various temperatures			
Preparative method	Dried under IR lamp	200°C	500°C	900°C	1400°C
Hydrothermal/H_2O[1]	Tet.^{r} 45^m	Tet.^{r} 45^m	Tet.^{r} 42^m	92^m	100^m
Hydrothermal/NH_4OH pH 10	Tet.^{r} 20^m	Tet.^{r} 26^m	Tet.^{r} 28^m	57^m	100^m
Hydrothermal/HCl pH 1	100^m	100^m	100^m	100^m	100^m

Notes. 1, See Fig. 4; tet., tetragonal zirconia; r, phase determined by Raman spectroscopy; m, percentage of monoclinic zirconia present in sample (accuracy $+/- 3$ mol%) by method of Ref. (21).

zirconium(IV) acetate, since both are likely to consist of the tetrameric species; this structural similarity may be relevant to the reaction process. The presence of high concentrations of chloride ions is known (38) to disrupt the polymerization of the tetrameric species. In this case the polymerization process does not occur but oxozirconium(IV) chloride forms instead. The X-ray amorphous material which formed after heating the gel at 200°C may be assumed to be a chloride-containing hydrous zirconia, which converts to tetragonal zirconia at 500°C. The transformation of $ZrOCl_2 \cdot xH_2O$ to tetragonal ZrO_2 via an amorphous phase has been associated with initial dehydration processes (7) and has been studied in detail (42). This transformation is evident in the X-ray powder diffraction patterns shown in Figs. 3a–3c,

with the further transformation to monoclinic zirconia at higher temperatures being revealed in Figs. 3d and 3e. It is seen from Table 1 that the partial conversion to monoclinic zirconia on being heated to 900°C is less complete for solids derived from solutions with low pH; this presumably reflects the poorer crystallinity of the $ZrOCl_2 \cdot xH_2O$ produced in such cases.

Zirconia Prepared by Hydrothermal Processing of Zirconium(IV) Acetate Solution

In contrast to the materials produced by boiling solutions under reflux, the dried white powders formed by hydrothermal processing were, without being heated further,
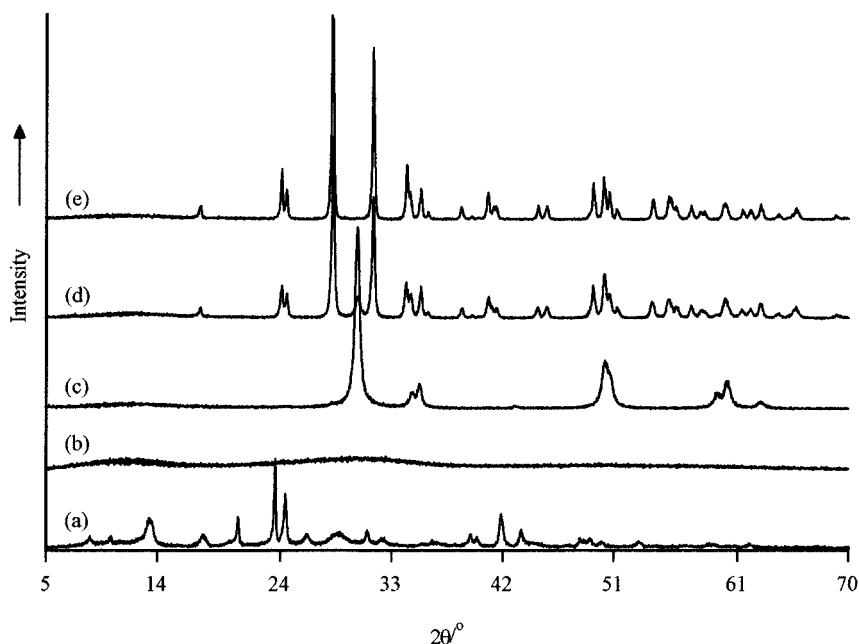
FIG. 3. X-ray powder diffraction patterns recorded from the reaction products which were produced by boiling an aqueous solution of zirconium(IV) acetate containing hydrochloric acid under reflux and then (a) dried under an infrared lamp and heated at (b) 200, (c) 500, (d) 900, and (e) 1400°C.
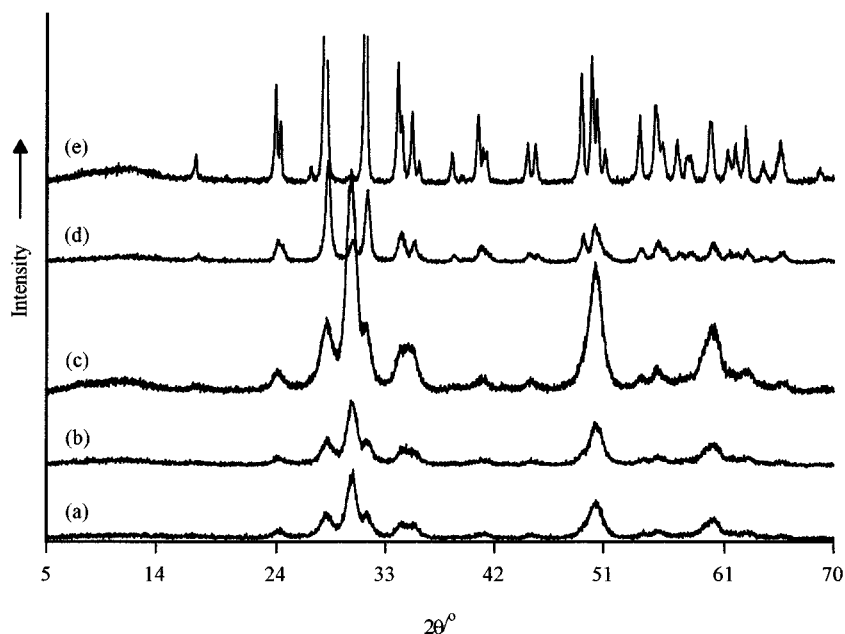
FIG. 4. X-ray powder diffraction patterns recorded from the reaction products which were produced by hydrothermally processing an aqueous solution of zirconium(IV) acetate which was then (a) dried under an infrared lamp and heated at (b) 200, (c) 500, (d) 900, and (e) 1400°C.

found to contain monoclinic zirconia. The proportion of monoclinic to tetragonal zirconia remained constant within measurement error on calcination at temperatures up to 500°C. Calcination at higher temperatures induced further conversion from the tetragonal to the monoclinic phase, to an extent which was dependent upon conditions, but which was complete in all cases after heating to 1400°C. This is apparent in Fig. 4, which shows the X-ray powder diffraction patterns of the products obtained from the aqueous solution.

The adjustment of the aqueous zirconium(IV) acetate solution to pH = 10 before hydrothermal processing resulted in a stabilization of the tetragonal phase, similar to that found in samples prepared by boiling the solution under reflux. A more striking contrast between the preparative methods is obtained if the solution has been adjusted previously to pH = 1: the material produced by hydrothermal processing was found, by X-ray powder diffraction, to be monoclinic zirconia, with no evidence for the tetragonal or cubic phases. Calcination at temperatures up to 1400°C resulted in enhanced crystallinity. It is likely that any oxozirconium(IV) chloride or tetragonal zirconia formed in the autoclave is a transient species which is not detected. Indeed, oxozirconium(IV) chloride was produced when the zirconium(IV) acetate solution was hydrothermally processed at 160°C and 2–3 bar pressure, which supports the notion that this compound exists as a transient species during processing at higher temperature.
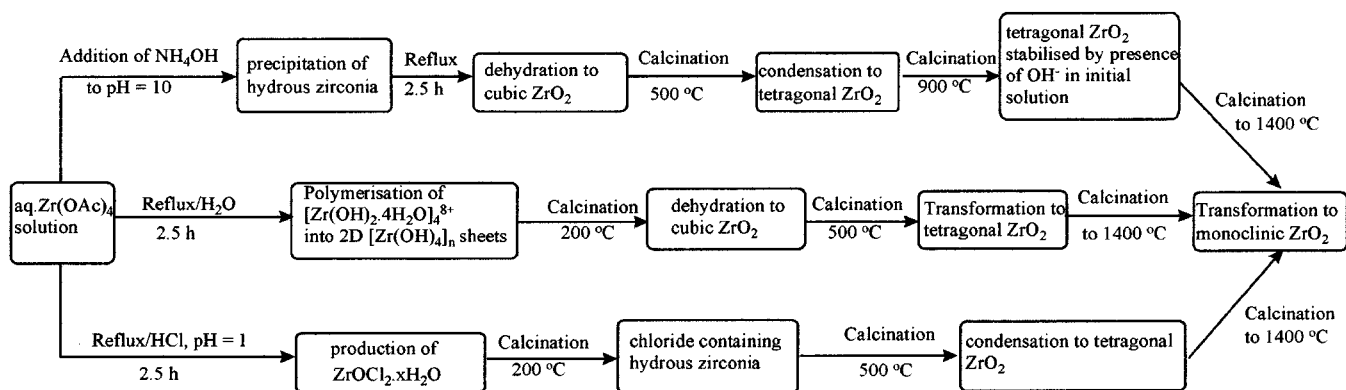

FIG. 5. Summary of phases formed from aqueous zirconium(IV) acetate after having been boiled under reflux.
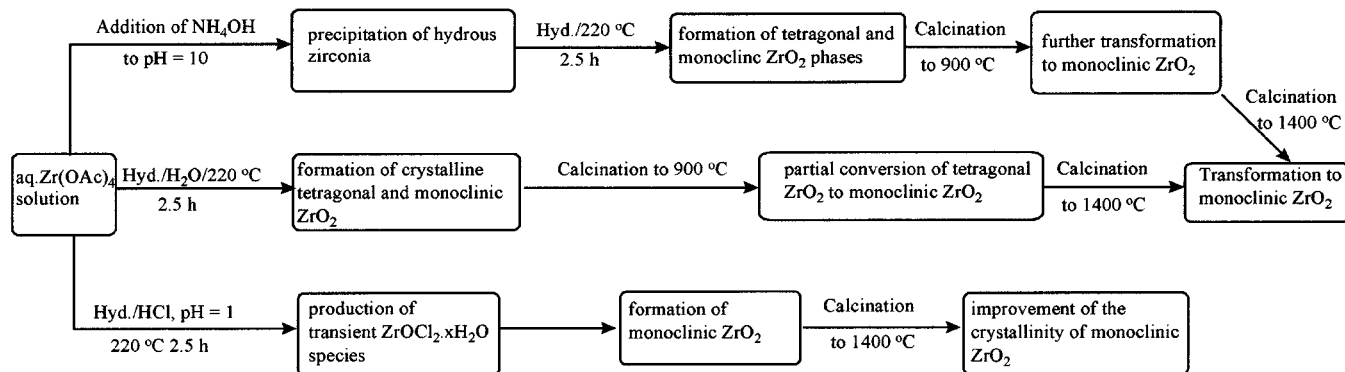
FIG. 6. Summary of phases formed from aqueous zirconium(IV) acetate after having been hydrothermally processed.

The results for the hydrothermally processed samples differ from those reported previously (12), viz. that the maximum formation of tetragonal zirconia is achieved at intermediate pH. The essentially amorphous powder removed from the autoclave after hydrothermal processing of aqueous zirconium(IV) acetate should be similar to that described as containing monoclinic zirconia nuclei (43). Alternatively the hydrolytic polymerization of aqueous $[Zr(OH)_2 \cdot 4H_2O]_4^{8+}$, which is likely to occur in the autoclave, gives a relatively unstable tetragonal phase which transforms to the monoclinic polymorph under the temperature and pressure which exist during the hydrothermal processing. At the present time it is not possible to distinguish between these two possibilities; however, the direct formation of monoclinic zirconia in the product from the autoclave indicates that the high pressure combined with the higher temperature associated with the hydrothermal treatment is critical for the formation of monoclinic zirconia under these conditions. Whether or not small particle size (5) also influences the preferential formation of monoclinic zirconia during the hydrothermal processing also requires investigation.

CONCLUSION

The pH of the reaction mixture is evidently an important variable in the production of zirconia from zirconium(IV) acetate solution, as is the method of processing.

Evaporated solutions of zirconium(IV) acetate boiled under reflux give, on calcination at increasing temperature, the progressive development of cubic, tetragonal, and finally monoclinic polymorphs of zirconia. Addition of HCl to the zirconium(IV) acetate solution gives the initially hydrated oxozirconium(IV) chloride. The amount of monoclinic zirconia formed by calcination at 900°C is influenced by the pH of the reaction mixture. The addition of aqueous ammonia stabilizes the tetragonal phase against conversion to the

monoclinic polymorph at temperatures up to ca. 900°C. The results are summarized in Fig. 5.

Hydrothermal processing of a solution of zirconium(IV) acetate gives a powder containing tetragonal and monoclinic zirconia, which is converted to monoclinic zirconia on calcination at temperatures exceeding 900°C. Addition of HCl to the zirconium(IV) acetate solution results in the formation of pure monoclinic zirconia via an oxozirconium(IV) chloride phase. In contrast, addition of ammonia to the zirconium(IV) acetate solution gives initially a mixture of tetragonal and monoclinic zirconia which, on calcination at temperatures exceeding 500°C, is converted to monoclinic zirconia. The results are summarized in Fig. 6.

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