

Influence of zirconium salt precursors on the crystal structures of zirconia

Ram Srinivasan and Burtron H. Davis

University of Kentucky, Center for Applied Energy Research, 3572 Iron Works Pike, Lexington, KY 40511, USA

Received 14 January 1992; accepted 15 April 1992

Procedures have been developed for preparing zirconia to yield either tetragonal or monoclinic phases following low (400–600°C) temperature calcination. The data in this note emphasize the need for paying attention to the precursor zirconium salt in preparing the monoclinic or tetragonal phases. A salt precursor obtained from a supplier at different times may produce different results. Generally, it is more difficult to obtain a precursor that will produce the monoclinic phase than the one that will produce the tetragonal form.

Keywords: Zirconium salt precursors; zirconia crystal structures

Recent research interests in zirconia ceramics have greatly enhanced the prospects for applying this material in catalysts, automotive gas sensors, etc. Zirconia has outstanding mechanical properties. Its complex chemical properties that include simultaneously reducing, oxidizing, acidic and basic properties make zirconia an attractive material for catalysis [1]. Recently, zirconia impregnated with sulfate ions has been claimed to exhibit superacidic behavior and to show high activity for isomerization of hydrocarbons [2–4]. Tanabe [1] attributed this behavior to superacid sites generated between the oxide and sulfate ions.

Hydrous zirconia was prepared by precipitating as a hydrous oxide from a solution of zirconium salt at different pH [5]. The $\text{Zr}(\text{NO}_3)_4$ salt that was obtained from Alfa Products, Morton Thiokol, Inc., in 1982 yielded a final product that was consistent with the phase expected [5]. Predominantly monoclinic phase was obtained by rapid precipitation at a pH of 10.5 using an excess amount of 15 N NH_4OH ; essentially pure tetragonal phase was produced if precipitated at a pH of 13–14 using either KOH or NaOH [5]. Since 1984, this source of $\text{Zr}(\text{NO}_3)_4$ has not been available. In our hands, using other sources of salts led to inconsistent results. Several requests for details of the preparation procedures we employed have been obtained following failure of an investigator to prepare a particular zirconia phase following our procedure. So far, little or

no attention had been paid to the source of the zirconium salt used in the preparation of the material. The objective of this manuscript is to emphasize the effect of the zirconium salt precursor in determining the crystalline phase of the final product.

Several zirconium salt precursors were used in this study. All of the precursors were dissolved in distilled/deionized water to make a zirconium salt solution of about 0.3–0.4 M concentration. An excess amount of 15 N NH_4OH was dumped into the salt solution, while vigorously stirring. Precipitation occurred at a pH of 10–10.5 in all cases. The precipitate was then washed thoroughly to peptization. In cases where a chloride salt was used, washing was carried out until a negative test for Cl^- ions was obtained using a silver nitrate solution. The washed precipitate cake was dried overnight at 120°C in air. After

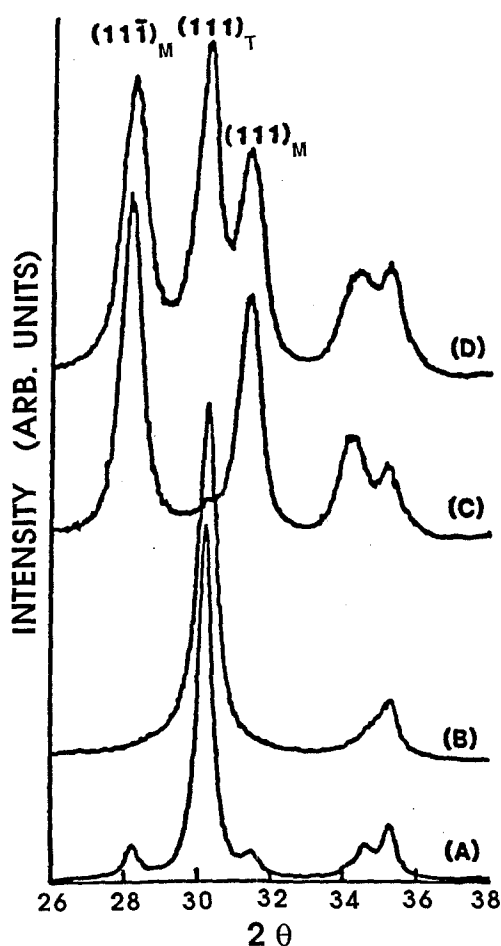


Fig. 1. X-ray diffraction patterns of ZrO_2 after calcination at 500°C for 4 h. ZrO_2 was prepared from several salt precursors at a pH of 10.5. (A) ZrOCl_2 (Alfa); (B) $\text{ZrO}(\text{NO}_3)_2$ (Alfa, 1989); (C) $\text{Zr}(\text{NO}_3)_4$ (Alfa, 1982); and (D) $\text{ZrO}(\text{NO}_3)_2$ in HNO_3 solution (Magnesium Elektron, Inc.).

drying, the granules were ground to a fine powder, and calcined at 500°C for 4–5 h in air in a muffle furnace. The sample was cooled to room temperature in air, and the crystal structures of the calcined materials were analyzed by X-ray diffraction.

The X-ray diffraction patterns of zirconia obtained from several zirconium salt precursors are shown in fig. 1. The material obtained from $\text{ZrOCl}_2 \cdot 4\text{H}_2\text{O}$ (Alfa Products, Morton Thiokol, Inc., 1985) yielded about 10% monoclinic phase and 90% tetragonal phase (curve A). The zirconium nitrate $\text{Zr}(\text{NO}_3)_4$ obtained from Alfa Products in 1982 yielded a material of nearly pure monoclinic phase (curve C); however, the nitrate salt supplied by this vendor in the following years produced materials that led to essentially pure tetragonal phase (curve B). A zirconium oxynitrate sample dissolved in nitric acid giving about 20% ZrO_2 in solution, was supplied by Magnesium Elektron, Inc. The XRD pattern of the material obtained from this latter source is shown as curve D in fig. 1; using this starting material led to about 50% each of monoclinic and tetragonal phases.

Anhydrous zirconium tetrachloride (ZrCl_4) was obtained from Alfa Products, Morton Thiokol, Inc. This highly hygroscopic salt was dissolved in water to produce about 0.3 M zirconium salt solution. This salt consistently yielded a material which, after calcination, showed about 90% monoclinic phase if the precipitation was rapid, and about 95% tetragonal phase if precipitated slowly [6]. The XRD patterns from these materials are shown in fig. 2. Using this salt, either the monoclinic or tetragonal phase could be prepared consistently.

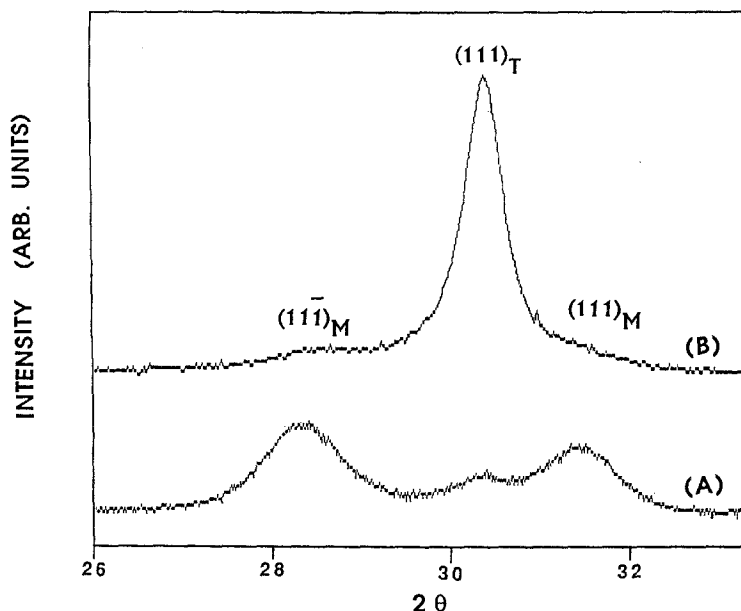


Fig. 2. X-ray diffraction patterns of ZrO_2 prepared from an anhydrous ZrCl_4 salt precursor supplied by Johnson Matthey Alfa Products. (A) Rapid precipitation, and (B) slow precipitation.

We purchased a source of $\text{ZrO}(\text{NO}_3)_2$ from Aldrich Chemical Company, Inc., in 1991. This salt was found to be at least partially insoluble in water and produced a turbid suspension in distilled water even after it was warmed to about $60\text{--}70^\circ\text{C}$. When concentrated HNO_3 was added to the turbid suspension, there was little, if any, change in the amount dissolved. This suspension was filtered during a period of 2–3 days, and concentrated ammonium hydroxide was dumped into the filtrate (although not a completely clear solution) to produce a pH of 10.5. After drying, the material appeared glassy, hard, and light greenish in color. This material, after calcination at 500°C for 5 h, was nearly pure tetragonal phase (fig. 3a). Zirconium oxynitrate ($\text{ZrO}(\text{NO}_3)_2$) salt was

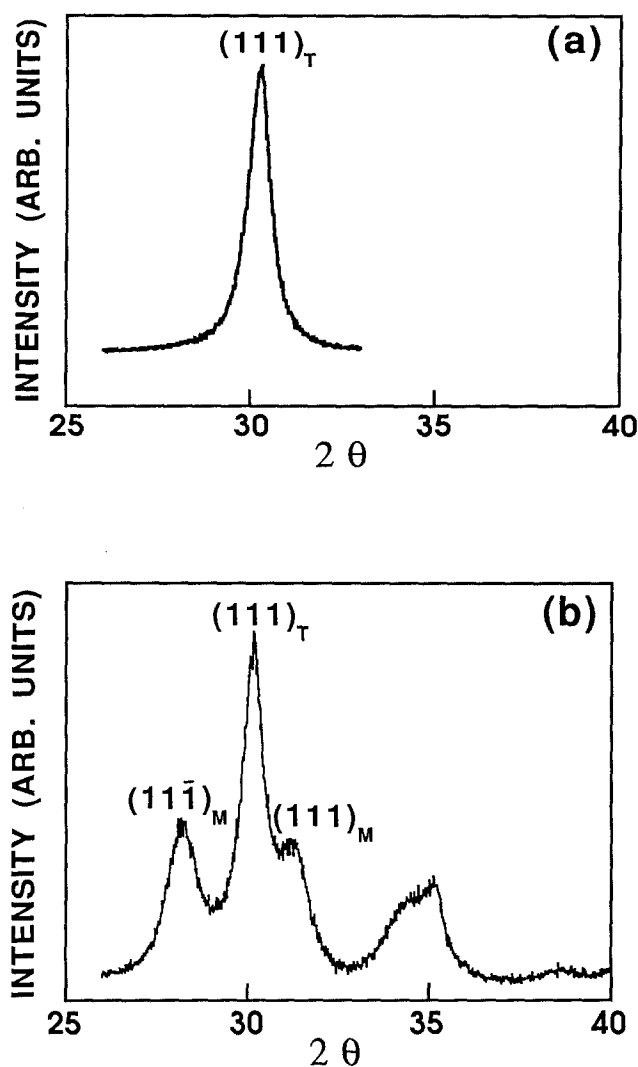


Fig. 3. X-ray diffraction pattern of ZrO_2 prepared from a $\text{ZrO}(\text{NO}_3)_2$ salt precursor obtained from Aldrich Chemical Company, Inc., in (a) 1991 and (b) 1990.

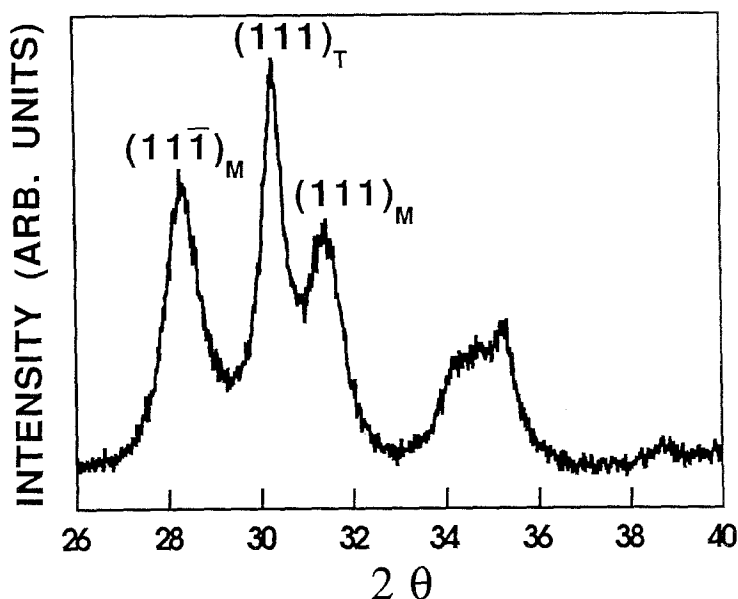


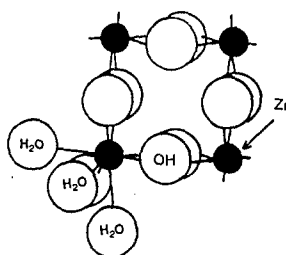
Fig. 4. X-ray diffraction pattern obtained from zirconia prepared from a zirconium sulfate precursor.

obtained from Aldrich in 1990, and this one was soluble in water. A 0.3 M solution prepared from this salt was rapidly precipitated with an excess of 15 N NH_4OH at a pH of 10.5. After calcination at 500°C for 4 h, this material exhibited a mixture of tetragonal and monoclinic phases (fig. 3b). Thus, a zirconium salt supplied by the same company at different times yielded a final product with different ratios of crystal phases even though the same preparation procedure was employed.

$\text{Zr}(\text{SO}_4)_2$ (also listed as ZrOSO_4) was obtained in 1992 from Aldrich Chemical Company, Inc. Attempts to prepare a material with the monoclinic phase by rapid precipitation with NH_4OH at a pH of about 10.5 was not successful. The material following calcination at 500°C for 4 h, was a mixture of the monoclinic and tetragonal phases (fig. 4).

The solution chemistry of zirconia is complex and not well understood. Depending upon the pH, a variety of chemical species may be present in the solution, which include polymeric materials [7]. Evidence has been presented to support the presence of a hydrated zirconium tetramer species [8] (scheme 1).

Under either hydrothermal aging at low ($< \text{about } 3$) pH or by increase in pH conditions, high molecular weight "hydrous zirconium oxide" polymers are formed. Dehydration of these "hydrous zirconium oxide" species leads to zirconia, which is reasonably insoluble. In natural ores, zirconium is present in a polymeric metal salt or in oxide form. To recover zirconium, the ores are subjected to various chemical treatments to render the Zr in a soluble form.



Scheme 1.

Very severe conditions are utilized to “depolymerize” the structures present in the ore, and it is believed that many of the processes do not affect depolymerization to a monomeric unit containing only one Zr. It is believed that most, or all, zirconium salts, except anhydrous ZrCl_4 , that are available from chemical companies, are predominantly comprised of polymeric species containing several Zr atoms.

In conclusion, the zirconium salt precursor has a tremendous influence on the resulting crystal structure of the calcined materials. It is proposed that the zirconyl salt may consist of polymeric clusters, and when this is the case it invariably leads to a high percentage of the tetragonal phase. When control of pH and time taken to effect precipitation are the variables employed to prepare the monoclinic form, a monomeric zirconium species should be used to prepare the solution. The importance of the starting zirconium salt has been repeatedly overlooked in the preparation of hydrous zirconia, and this is a likely source for many of the diverse results that have been reported so far.

Acknowledgement

This research was funded by the Commonwealth of Kentucky and the US D.o.E. (contract No. DE-AC22-90PC90049).

References

- [1] K. Tanabe, *Mat. Chem. Phys.* 13 (1985) 347.
- [2] M. Hino, and K. Arata, *J. Chem. Soc. Chem. Commun.* (1980) 851.
- [3] K. Arata, M. Hino and N. Yamagata, *Bull. Chem. Soc. Japan* 63 (1990) 244.
- [4] M.Y. Wen, I. Wender and J.W. Tierney, *Energy and Fuels* 4 (1990) 373.
- [5] B.H. Davis, *J. Am. Ceram. Soc.* 67 (1984) C-168.
- [6] R. Srinivasan, M.B. Harris, S.F. Simpson, R.J. De Angelis and B.H. Davis, *J Mat. Res.* 3 (1988) 787.
- [7] C.F. Baes Jr. and R.E. Mesmer, *The Hydrolysis of Cations* (Wiley, New York, 1976) pp. 152–157.
- [8] A. Clearfield, *Inorg. Chem.* 3 (1964) 146.