THE EFFECT OF SULFATE ON THE CRYSTAL STRUCTURE OF ZIRCONIA

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Zirconia can be prepared to produce either tetragonal phase or predominantly monoclinic phase upon calcination at 500 °C. The precursors for each phase of zirconias was treated with 1N H_2SO_4 to produce a sulfated material. The results reveal that sulfation causes the tetragonal phase to be formed for both types of zirconia contrary to the data before sulfation, and sulfation increases the crystallization exotherm by 150 °C.

1. Introduction

Zirconium oxide is claimed to be the only metal oxide catalyst whose surface possesses four chemical properties: acidic, basic, oxidizing and reducing properties [1]. Primary uses of ZrO_2 in catalysis are the synthesis of isobutene or methanol from carbon monoxide and hydrogen [2,3], hydrogenation of butadiene with H_2 and H-D exchange [3–7], isomerization of 1-butene [8], dehydration of alcohols, especially production of α-olefins from 2-alcohols [9,10], etc. The activity and selectivity of zirconia catalysts are significantly influenced by the preparation methods and the activating treatments of these catalysts [10,11]. Sulfate-promoted zirconias have been shown to exhibit superacid behavior and to exhibit a high activity for isomerization of hydrocarbons [12–14] or for conversion of methanol into hydrocarbons [15]. Tanabe [1] suggested that the superacidic sites are generated by the interaction between the oxide and sulfate ions. It was also reported that the transition of the amorphous to crystalline phase was disturbed [16].

It was recently reported that the rapid precipitation of zirconium tetrachloride ($ZrCl_4$) with ammonium hydroxide at pH 10.5 yielded predominantly monoclinic phase and a slow precipitation (8 hours) produced the tetragonal phase upon calcination at 500 °C [17]. The objective of this paper is to observe the effects of sulfation on these two types of zirconias which produce two different crystal

structures when calcined, and to relate them to the crystal chemistry of the sulfated zirconia.

2. Experimental methods

Sample m-ZrO$_2$ was prepared by rapid precipitation of anhydrous zirconium tetrachloride solution with excess of ammonium hydroxide at pH 10.5. The precipitate was extensively washed with distilled-deionized water, and dried at 120°C for about 30 hours. Sample t-ZrO$_2$ was prepared from ZrCl$_4$ solution by a slow precipitation method; i.e., the amount of base required to give a pH of 10.5 was added dropwise during 8 hours to the zirconium salt solution, while vigorously stirring the mixture [17]. The white precipitate was washed extensively, and dried at 120°C for about 30 hours. After drying, the powders were ground in a mortar and pestle and used for the studies described below.

The m-ZrO$_2$ and t-ZrO$_2$ powders were sulfated following a procedure described by Yamaguchi et al. [16]. The impregnation with H$_2$SO$_4$ was performed by immersing 5 g of m-ZrO$_2$ or t-ZrO$_2$ in 30 ml of 1N H$_2$SO$_4$ for 1 hour at room temperature, filtering, and drying at 120°C for 20 hours. These sulfated samples were designated as m-ZrO$_2$-S and t-ZrO$_2$-S. This procedure is reported to incorporate about 3 wt% SO$_4^{2-}$ [1]; however, in our case this procedure resulted in the incorporation of ca. 9.1 $\pm$ 0.2 wt.% sulfate for each ZrO$_2$ sample.

The m-ZrO$_2$ and t-ZrO$_2$ powders were calcined at 500°C for 5 hours. Following calcination, each zirconia had a surface area of 90 $\pm$ 5 m^2/g. The crystalline phases were determined using a Rigaku X-ray diffractometer. The radiation used was CuKα, with an oriented pyrolytic graphite monochromator on the diffracted beam path. The diffraction data were acquired at a step width of 0.02°, counting 10 sec at each step in the 2θ region of interest.

Thermal analyses were conducted on a Seiko model TG/DTA 320. Both DTA and TGA data were obtained simultaneously from the dried zirconia samples at a heating rate of 20°C/min, in a helium flow.

3. Results and discussion

The objective of this paper is to learn whether the phase transition from amorphous to crystalline form at about 400–500°C in ZrO$_2$ is a surface or bulk phenomenon, and to identify how the sulfate ions influence the crystal structure of zirconia.

The XRD patterns of m-ZrO$_2$ and t-ZrO$_2$ are shown in fig. 1. After calcination at 500°C for 5 hours, the m-ZrO$_2$, which was rapidly precipitated at 10.5 pH, exhibits predominantly monoclinic structure, and t-ZrO$_2$, which was precipitated during an 8 hour period, shows tetragonal structure. Thus, we have established a
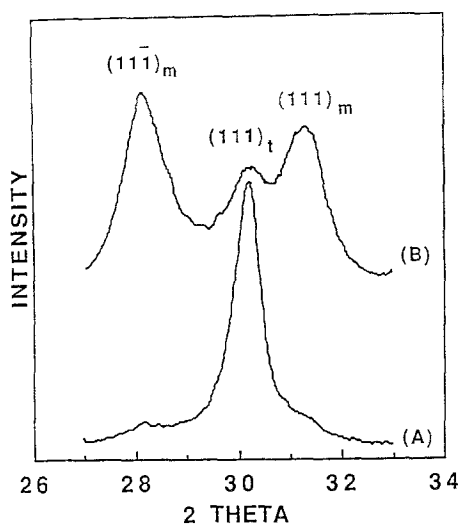
Fig. 1. X-ray diffraction patterns obtained from (A) t-ZrO_2 and (B) m-ZrO_2.

procedure to produce m-ZrO_2 or t-ZrO_2 crystal seeds at 10.5 pH. This procedure is reproducible when the zirconyl solution is prepared from anhydrous $ZrCl_4$; however, if other zirconyl salts were used, the final product from the rapid precipitation is frequently a mixture of t-ZrO_2, and m-ZrO_2 [18]. It is believed that it is necessary to begin with a monomeric Zr^{4+} species, or a polymeric Zr species that contains only a limited number of Zr^{4+} species. Most zirconyl salts sold commercially apparently contain higher polymeric zirconium species that primarily produce t-ZrO_2.
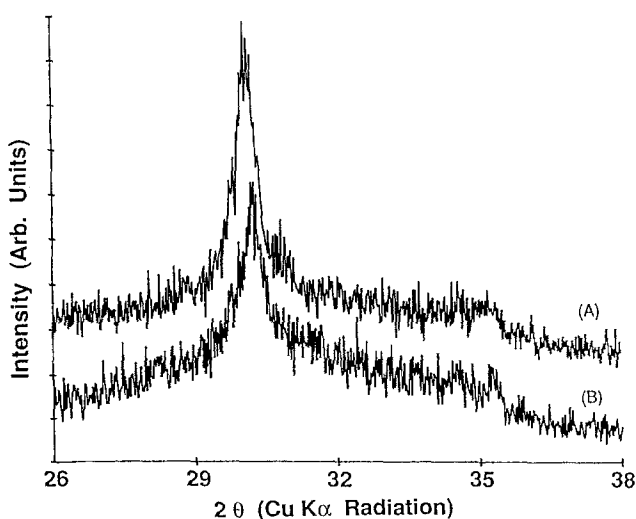

Fig. 2. X-ray diffraction patterns from (A) t-ZrO_2-S and (B) m-ZrO_2-S.
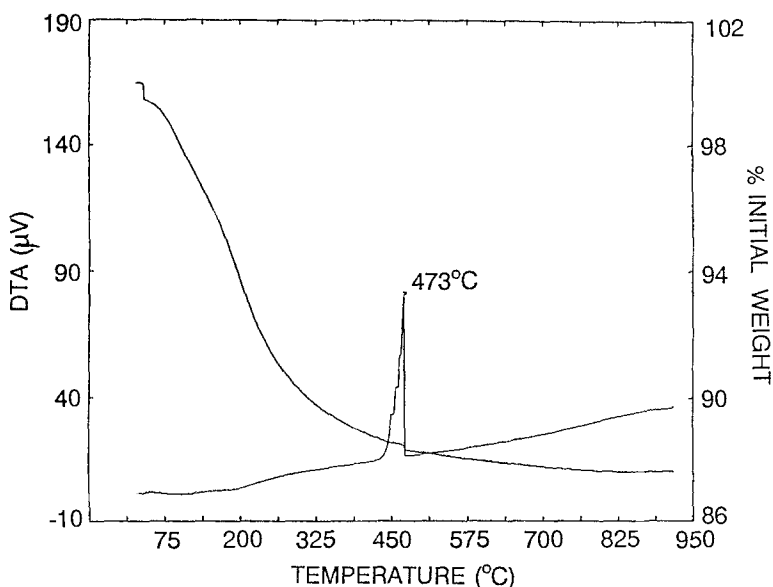
Fig. 3. DTA/TGA curves for m-ZrO$_2$ at a heating rate of 20°C/min. in helium.

The line width for the XRD peaks in fig. 1A and B are different. We have shown that when tetragonal zirconia transforms to monoclinic zirconia the X-ray crystallite size decreases; this has been shown to be due to the formation of multiply twined crystals during the transformation [19,20].

The XRD patterns of the sulfated zirconias are shown in fig. 2, wherein it can be observed that sulfation produces zirconia of tetragonal phase only. Both m- and t-ZrO$_2$ exhibited a crystallization exotherm at about 450°C (a typical plot for m-ZrO$_2$ is shown in fig. 3), and the heat evolved was the same irrespective of the final crystal structure produced [17]. However, the exotherm peak was shifted to 607°C for m-ZrO$_2$-S and to 590°C for t-ZrO$_2$-S (fig. 4). This result is consistent with that of Yamaguchi et al. [16]. It was reported that the presence of SO$_4^{2-}$ is in some way responsible for inhibiting the crystallization of ZrO$_2$ while retaining a much greater fraction of the original specific surface area [21]. Yamaguchi et al. [16] reported that the SO$_4^{2-}$ anions reduced the exotherm peak amplitude and shifted the peaks to higher temperatures and thus seems to disturb the phase transition. However, the mechanism by which the sulfate anions can retain the surface area and at the same time disturb the phase transition is not clear.

TGA analysis shows no significant weight loss occurred during the small temperature range of the exotherm; this was true for both m-ZrO$_2$ or t-ZrO$_2$. It appears that most of the small weight loss at the exotherm in this and probably other studies is due to loss of sample from the holder due to violent fracture of the particles during crystallization. The four samples (m-ZrO$_2$, t-ZrO$_2$, m-ZrO$_2$-S and t-ZrO$_2$-S) all lose about 10 to 12% of their initial weight by the time they
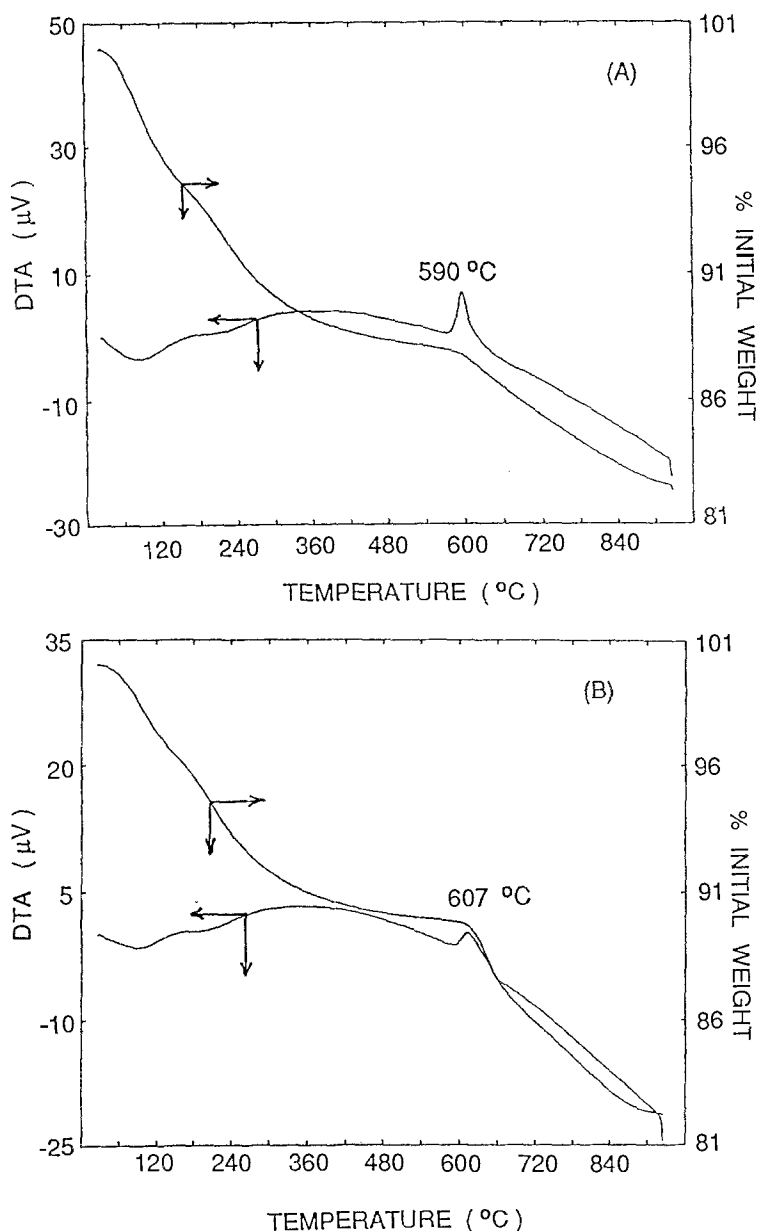
Fig. 4. DTA/TGA curves for the (A) t-ZrO$_2$-S and (B) m-ZrO$_2$-S (same conditions as used to generate curves shown in fig. 3).

have been heated to the exotherm temperature. Heating the m-ZrO$_2$ sample from the exotherm temperature (473°C) to 900°C results in little additional weight loss (fig. 3); data similar to that of fig. 3 was obtained for t-ZrO$_2$. In contrast, heating either m-ZrO$_2$-S or t-ZrO$_2$-S above the exotherm temperature results in further weight loss. The data in figs. 4A and 4B indicate that an additional weight

loss of 7 to 9 wt.% resulted upon heating either sulfated sample from the exotherm temperature to 900 °C. The agreement between the higher temperature weight loss and the amount of SO_4^{2-} present (9.1 wt.%) is reasonable; if all of the sulfur is lost as SO_2 the 9.1 wt.% SO_4 would correspond to a weight loss of ca. 6.1 wt.%. The total weight loss between the exotherm temperature and 900 °C would then correspond to loss of all of the sulfur and ca. 2 wt.% water as was observed with the unsulfided zirconias.

The retention of the metastable t-ZrO_2 phase has been attributed to crystallite size; according to this view, differences in surface energy of the m- and t-ZrO_2 causes t-ZrO_2 to form when the crystals are below a minimum size. However, the crystallite size is not the primary factor responsible for the difference between the crystal phase for m-ZrO_2 and m-ZrO_2-S. Both m-ZrO_2 and m-ZrO_2-S are formed from a common precursor so that initially the two samples have the same particle size. Heating the precursor that does not contain SO_4^{2-} produces a material with the monoclinic phase; heating the precursor containing the surface SO_4^{2-} leads to the tetragonal phase even after heating to 600 °C. Both materials have similar surface areas after calcination at 500 °C. The sulfate added to the surface of the precursor therefore retards the formation of the monoclinic phase.

The data suggest that the adsorbed sulfate ion is responsible for altering the thermal conversions of m-ZrO_2 from the normal pathway. It appears that the tetragonal phase results for the sulfate containing materials whether the precursor used as starting material was m-ZrO_2 or t-ZrO_2. This implies that surface, and not bulk, effects are the dominant factor in the t → m transformation.

Acknowledgment

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