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# The influence of preparation conditions on the surface area of zirconia

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## Abstract

The conditions for preparation of high surface area zirconia were studied. Samples were prepared by precipitation from aqueous solutions of zirconium chloride with ammonium hydroxide. The order of addition of the reactants was found to affect the surface area. Digestion of the hydrous zirconia is the key to high surface area zirconia without the necessity of adding other oxides or dopants. Both the temperature and the time of digestion are important parameters. Zirconia with surface area in excess of 220 $m^2/g$ after calcination at 500°C have been obtained. The materials maintained a surface area of $> 90$ $m^2/g$ even after heat treatment at 900°C for 12 h. In addition, digestion led to the formation of the tetragonal allotrope of zirconia. Samples which had been digested for long times at 100°C are tetragonal and maintain this phase up to 1000°C. The effects of digestion seems to be related to a phase transformation of the hydrous precursor at around 80°C. A mechanism based on defect density is postulated to explain the phase stability.

## 1. Introduction

Zirconium oxide and compounds containing zirconium are increasingly being recognized as useful catalytic materials. In particular, zirconium oxide (zirconia) is an important support material for catalysis, having both acidic and basic properties. From adsorption measurements of $CO_2$ and $NH_3$ on zirconia calcined at 600°C, the number of acid and basic sites was found to be ca. 0.6 $\mu mol/m^2$ and 4 $\mu mol/m^2$, respectively [1]. Zirconia has a high melting point of about 2700°C and is stable even under reducing conditions. Unlike titania, it

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does not form reactive electron-hole pairs under photo irradiation. All these make it a useful support even under harsh conditions. Zirconia can also function as a catalyst by itself. For instance, it catalyses the hydrogenation of CO [2,3], olefins [4] and dienes [5]. In the Fischer–Tropsch synthesis of higher hydrocarbons from synthesis gas, the addition of zirconia to catalysts containing cobalt and silica resulted in excellent activity and selectivity for the production of long chained hydrocarbons, which can be subsequently hydrotreated to give synthetic petroleum, diesel or aviation fuel [6]. The incorporation of zirconia into the automotive catalyst improves the thermal stability and reduces the migration of rhodium into the alumina lattice. Sulphated zirconia is a solid superacid which catalyzes a number of reactions such as alkylation, acylation and isomerisation reactions [7,8]. Excellent yields were noted with the use of sulphated zirconia.

The use of zirconia as a catalyst or as a support is effective only when the compound has a high surface area which remains stable under process conditions. Various methods have been described in the literature to obtain high surface areas or nanosize zirconia. Ozawa and Kimura [9] impregnated active carbon made from coconut char (surface area 2400 $m^2/g$) with aqueous zirconyl nitrate. Subsequent pyrolysis and burn-out at 550°C resulted in zirconia powder with a surface area of 150 $m^2/g$. Inoue et al. [10] reported on the preparation of zirconia with surface area of 90–150 $m^2/g$ (calcined at 500°C) from zirconium alkoxides in organic solvents like glycols and toluene under hydrothermal conditions. Another group used the slow release of a base by a chemical reaction [11,12]. Zirconia with a well-developed mesoporous texture was obtained by gel-precipitation [13,14]. The average pore diameter increases from ca. 3.16 to 20.6 nm as the calcination temperature was raised from 450°C to 850°C. The surface area after calcination at 450°C for 15 h was 111 $m^2/g$.

Higher surface areas can be obtained with sulphated zirconia [15,16] or when zirconia is partially substituted with other oxides such as lanthanum oxide, magnesium oxide, calcium oxide or yttrium oxide [17,18]. The incorporation of other oxides or sulphates leads to the tetragonal form of zirconia. This partially stabilized zirconia is used as structural ceramic material. In the stress field of a propagating crack, a martensitic transformation of the tetragonal particles to the monoclinic form results. This transformation is accompanied by a volume increase, closing the crack. Hence partially stabilized zirconia finds commercial application due to their high strength and toughness.

In a previous communication [19], we reported on some preliminary results which showed digestion to be a key step in the preparation of high surface area zirconia. More studies have since been performed to optimize the synthesis. We report here on the different parameters during preparation which influence the surface area, i.e., time and temperature of digestion, order of precipitation, and effect of lanthanum oxide addition.

## 2. Method

### 2.1. Preparation of zirconia

Hydrous zirconia was obtained by hydrolysis of zirconium(IV) chloride (Merck) with a base. 5 M ammonium hydroxide was used in this study. The zirconium hydroxide formed as a gelatinous precipitate. In fact, the initial purpose of digesting the precursor was to improve its filterability. This has led to the surprising observation that the calcined product has a greatly increased surface area.

A ca. 10 wt.-% (approximately 0.43 M) aqueous solution of zirconium(IV) chloride was first prepared. This solution was added dropwise, with stirring, to a measured excess of 5 M aqueous ammonia (about 150% in excess). The pH was continuously monitored with a pH meter and found to decrease from 11.8 initially to about 9.4 at the end of precipitation. Hence, during the entire course of precipitation, the pH was in the basic range. The materials prepared by this route are identified as 'basic'. Preparations labelled as 'acidic' were carried out by adding 5 M aqueous ammonia dropwise to the zirconium chloride solution (pH < 1) until the pH of the resulting solution levelled off at 9.4. Excess ammonia was always used. During the precipitation, the viscosity of the gel formed reached a maximum at pH 4.5 before exhibiting a markedly reduced viscosity with further addition of ammonia. With more ammonia, the adsorption of ions of similar charge may take place on the surface of the colloidal particles so that there is repulsion, leading to decreased viscosity of the solution. No viscosity transition was observed in the gel prepared in basic media. For the lanthanum-doped series, an additional amount of lanthanum nitrate corresponding to the required final wt.-% was dissolved in the aqueous solution.

In total, four batches of hydrous zirconia were prepared: the first two by precipitation in basic media, the third by precipitation in acidic medium, and a fourth by precipitation in acidic media with lanthanum nitrate to give a final product with 3.5% lanthanum oxide (identified as 'acid-doped'). For the basic series, both the temperature of digestion and the length of digestion time were investigated. For the acidic and the acid-doped series, only the temperature of digestion was studied.

### 2.2. Digestion and calcination of hydrous zirconia

To study the effect of digestion temperature, each batch of precipitated hydrous zirconia was divided into five equal portions. One was left undigested and allowed to age at room temperature for 48 h (30°C) while the other four were digested in their mother liquor at 60°C, 70°C, 80°C and 100°C, respectively. Within the batch, the digestion time was kept constant at 48 h. To study the influence of digestion time, the hydrous zirconia was kept at a constant

temperature of 100°C, and the time of digestion was varied from 0, 6, 12, 24, 48 and 96 h. Additional ammonia was added throughout to maintain the pH at ca. 9.4.

The digested samples were vacuum filtered and washed thoroughly with a dilute solution of ammonium nitrate until the wash solution tested negative for chloride. The use of ammonium nitrate facilitates the washing and removes the chloride much easier than does deionized water. The samples were then dried overnight in an oven at 100°C before calcination in a muffle furnace. A slow heat ramp of 1°C/min was used to reach the calcination temperature (500–900°C) and the temperature was held for 12 h.

To identify the zirconia obtained from the different preparations, we use the following code: $X$-$T_D$-$y$h-$T_C$ where $X$ = A, B or AD for 'acidic', 'basic' or 'acid-doped' preparations, $T_D$ is the temperature of digestion, $y$h is the digestion time in hours, and $T_C$ is the calcination temperature.

## 2.3. Characterization

The surface area of the calcined samples was determined by nitrogen physisorption using a Micromeritics Flowsorb 2300. Before each measurement, the sample was degassed at 350°C for at least 30 min or until no more water was seen to desorb. The composition and crystallite size of the material were determined by powder x-ray diffraction (Philips PW 1729, Cu K$\alpha$ 1.5418 Å). Spectra over an extended range from $2\theta = 20°$ to $80°$ were taken at $4°$/min and a slow scan at $0.3°$/min was used to record the range from $2\theta = 27°$ to $33°$. The amount of tetragonal and monoclinic phase present in the zirconia was estimated by comparing the areas under the characteristic peaks of the monoclinic phase ($2\theta = 28.5°$ and $31.6°$ for the $(11\bar{1})$ and $(111)$ reflexes respectively) and the tetragonal phase ($2\theta = 30.4°$ for the $(111)$ reflex). Gaussian curves were first fitted to the x-ray diffraction pattern at the characteristic peaks and the height $h$ and half-width $w$ obtained therefrom. The percent composition of each phase was calculated from the Gaussian areas $h \times w$:

$$\% \text{ monoclinic} = \frac{\Sigma(h \times w)_{\text{monoclinic}}}{\Sigma(h \times w)_{\text{monoclinic and tetragonal}}} \tag{1}$$

$$\% \text{ tetragonal} = \frac{\Sigma(h \times w)_{\text{tetragonal}}}{\Sigma(h \times w)_{\text{monoclinic and tetragonal}}} \tag{2}$$

The crystallite size for each phase was estimated using the Debye–Scherrer equation:

$$D_{\text{hkl}} = \frac{0.9\,\lambda}{\beta_{\text{hkl}} \cdot \cos\theta} \tag{3}$$

where $D_{\text{hkl}}$ is the crystallite size, $\lambda$ is the wavelength of the Cu K$\alpha$ radiation, $\beta_{\text{hkl}}$ is the corrected peak width in radians calculated from $\beta = \sqrt{B^2 - b^2}$

where $B$ is the observed peak width and $b$ is the instrumental broadening, and $\theta$ is the Bragg diffraction angle.

## 3. Results

### 3.1. Effect of digestion temperature and preparation on surface area

The effect of temperature of digestion was tested on three series of zirconia prepared under acid, basic and acid-doped conditions. The surface area of the undigested samples, A-30-48h-500, B-30-48h-500 and AD-30-48h-500, was 32, 54 and 64 m$^2$/g, respectively (Fig. 1). If a higher digestion temperature was used, the surface area of the calcined zirconia increased. The increase was modest for digestion temperatures between 30 and 70°C. The surface area of samples digested at 70°C was 48 m$^2$/g for the A-preparation and about 70 m$^2$/g for the B and AD series. However, digestion at 80°C and above brought about a significant increase in the surface area. After digestion at 100°C, the surface area of the zirconia, A-100-48h-500, was 140 m$^2$/g, and as high as 225 m$^2$/g for the basic preparation. The doped material had a comparable surface area to the basic sample, at 221 m$^2$/g. Hence, the optimal temperature for digestion of the hydrous zirconia was found to be 100°C.

It is apparent from both Fig. 1 and Table 1 that the order of addition of the reagents during precipitation affects the surface area of the resulting zirconia. Over the range of digestion temperatures studied, the hydrous oxide precipitated
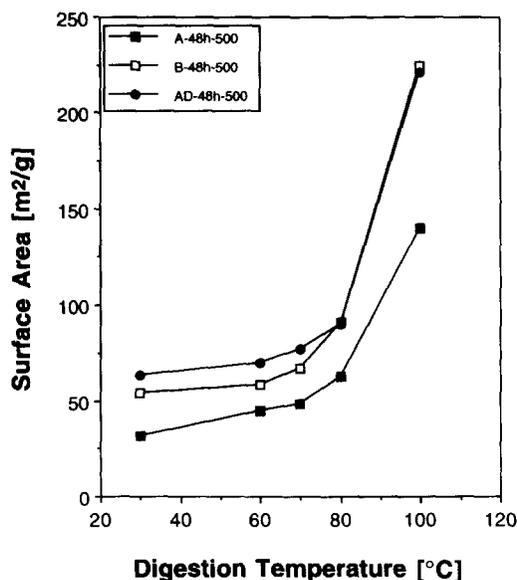


Fig. 1. Effect of digestion temperature on the surface area of zirconia prepared from the acidic, basic and acid-doped series. Calcination conditions: 500°C, 12 h.

Table 1
Surface area of samples prepared by acidic, acid-doped and basic methods

| Calcination temperature (°C) | Digestion temperature (°C) | Surface area | | |
|---|---|---|---|---|
| | | Acidic | Acid-doped (m²/g) | Basic |
| 500 | 30 | 31.9 | 63.3 | 54.2 |
| | 60 | 44.4 | 69.5 | 58.1 |
| | 70 | 48.5 | 76.9 | 66.7 |
| | 80 | 62.4 | 90.2 | 90.4 |
| | 100 | 140 | 221 | 225 |
| 600 | 30 | 23.6 | 51.4 | 32.5 |
| | 60 | 29.0 | 54.5 | 38.5 |
| | 70 | 37.0 | 58.7 | 46.3 |
| | 80 | 47.0 | 74.0 | 66.8 |
| | 100 | 114 | 154 | 155 |
| 700 | 30 | 17.7 | 39.1 | 25.6 |
| | 60 | 24.1 | 51.3 | 29.0 |
| | 70 | 29.9 | 53.3 | 35.4 |
| | 80 | 40.2 | 65.0 | 54.5 |
| | 100 | 92.8 | 137 | 134 |
| 800 | 30 | 11.8 | 24.3 | 20.3 |
| | 60 | 18.4 | 34.5 | 23.1 |
| | 70 | 23.6 | 34.3 | 30.2 |
| | 80 | 31.1 | 41.4 | 44.2 |
| | 100 | 64.1 | 108 | 101 |
| 900 | 30 | 9.69 | 20.4 | 14.4 |
| | 60 | 13.7 | 26.0 | 18.0 |
| | 70 | 16.9 | 26.3 | 21.4 |
| | 80 | 23.2 | 31.0 | 32.2 |
| | 100 | 32.2 | 73.9 | 65.6 |

Samples at 30°C were undigested.

under acidic conditions yielded zirconia with lower surface area than the basic process. For digestion temperatures below 70°C, the acid-doped oxides had the highest surface area of the three series. However, for digestion at 80°C and higher, the surface area of zirconia from the basic process was very similar to that to the acid-doped material. It is clearly advantageous to precipitate the hydrous zirconia in an excess of ammonium hydroxide so that a pH > 9 is maintained throughout the entire precipitation.

## 3.2. Effect of digestion time on surface area

The effect of digestion time was investigated at 100°C as this was found to be the most effective temperature for preparing high surface area zirconia. The
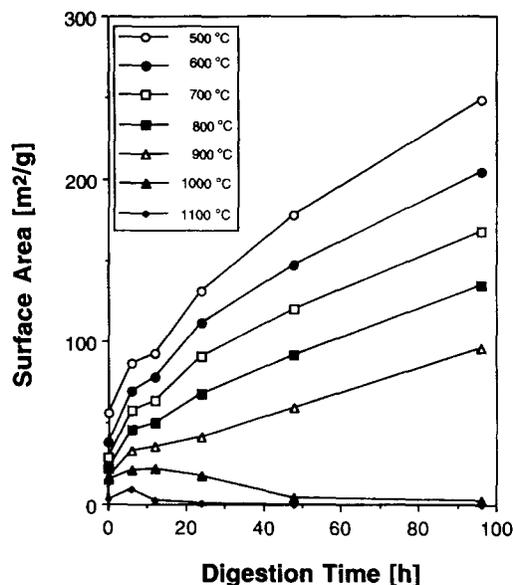
Fig. 2. Effect of time of digestion at 100°C on the surface area of zirconia. Heat treatment: 12 h at each temperature.

hydrous zirconia was precipitated under basic conditions by adding the zirconium chloride solution to ammonium hydroxide. The suspension was kept gently boiling under reflux and constant pH. Samples were withdrawn for analysis at fixed time intervals, washed, dried and calcined. The zirconia obtained from the hydrous oxide, which had been removed immediately after precipitation and which had not been subjected to any digestion, B-100-0h-500, has a surface area of 47.9 m$^2$/g. Upon digestion of the hydrous zirconia for 6 h at 100°C, the surface area of the calcined compound, B-100-6h-500, rose to 86.4 m$^2$/g. Increasing the digestion time further enhances the surface area of the final product (Fig. 2). The zirconia, B-100-96h-500, had an exceptionally high surface area of 248 m$^2$/g, a five-fold increase over the undigested sample.

## 3.3. Effect of digestion temperature and preparation on phase formation

Zirconia is polymorphic and can exist in the monoclinic, tetragonal, orthorhombic or cubic (fluorite) structure. The monoclinic phase is stable to ca. 1100°C, and transforms to tetragonal as the temperature increases to 1200°C. On cooling, this high-temperature tetragonal phase transforms to the monoclinic phase with a large hysteresis so that the tetragonal to monoclinic transition occurs between 1000°C and 850°C. It is possible to prepare metastable tetragonal zirconia at lower temperatures by precipitation from aqueous solutions or by thermal decomposition of zirconium salts.

Table 2
Percent tetragonal phase in samples prepared by acidic, acid-doped, and basic methods

| Calcination temperature (°C) | Digestion temperature (°C) | % Tetragonal phase | | |
|---|---|---|---|---|
| | | Acidic | Acid-doped | Basic |
| 500 | 30 | 11.3 | 100 | 22.8 |
| | 60 | 17.5 | 100 | 21.4 |
| | 70 | 27.3 | 100 | 21.4 |
| | 80 | 44.4 | 100 | 49.4 |
| | 100 | 100 | 100 | amorphous |
| 600 | 30 | 8.30 | 100 | 12.4 |
| | 60 | 10.2 | 100 | 15.2 |
| | 70 | 15.8 | 100 | 20.2 |
| | 80 | 36.5 | 100 | 45.5 |
| | 100 | 100 | 100 | 100 |
| 700 | 30 | 8.1 | 79.7 | 0.0 |
| | 60 | 11.5 | 80.7 | 5.6 |
| | 70 | 12.7 | 100 | 11.0 |
| | 80 | 30.3 | 100 | 31.7 |
| | 100 | 100 | 100 | 100 |
| 800 | 30 | 0.0 | 69.2 | 0.0 |
| | 60 | 0.0 | 70.4 | 0.0 |
| | 70 | 9.5 | 76.3 | 0.0 |
| | 80 | 17.2 | 82.4 | 24.6 |
| | 100 | 100 | 100 | 100 |
| 900 | 30 | 0.0 | 53.2 | 0.0 |
| | 60 | 0.0 | 68.7 | 0.0 |
| | 70 | 7.2 | 72.1 | 0.0 |
| | 80 | 17.2 | 82.7 | 16.3 |
| | 100 | 100 | 100 | 100 |

Samples at 30°C were undigested.

Besides the described enhancement in surface area, it was found that digestion also affected the structure of the resulting zirconia. For the acid and basic preparations, both monoclinic and tetragonal phases were found in all the samples digested below 100°C (Table 2). As with the surface area, the relative amount of each phase showed a dependence on the digestion temperature. Samples A-30-48h-500 and B-30-48h-500 showed the lowest amount of the tetragonal phase, the zirconia existing mainly in the monoclinic form. The proportion of tetragonal phase increases when the digestion temperature was raised from 70°C to 80°C. The zirconia A-100-48h-500 and B-100-48h-500 were purely tetragonal. Even after calcination to 900°C, these samples maintained the
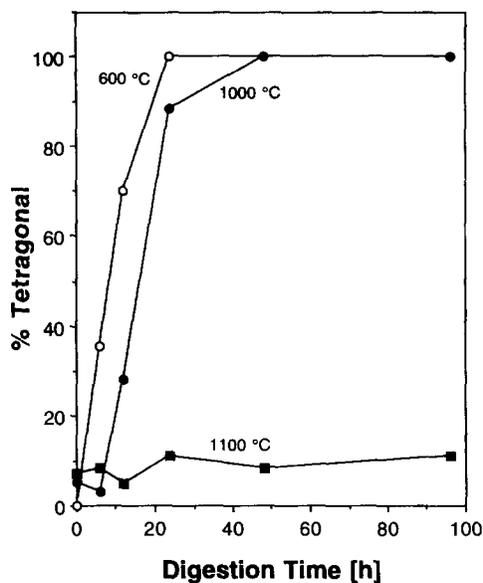
Fig. 3. Amount of tetragonal phase as a function of digestion time for zirconia, B-100-96h, heat treated to 600°C, 1000°C and 1100°C.

metastable tetragonal structure. However, zirconia prepared by digestion at lower temperatures showed increasing amounts of the monoclinic phase as the calcination temperature was raised. After heating to 800°C, samples A-30-48h-800 and A-60-48h-800 prepared by the acidic process were purely monoclinic. Likewise, samples from the basic route, B-30-48h-800, B-60-48h-800, B-70-48h-800, were purely monoclinic after calcination to 800°C. The acid-doped zirconia was purely tetragonal up to a calcination temperature of 600°C, irrespective of the digestion temperature. If the samples were heated to 700°C, the monoclinic phase starts to appear in samples digested at 30°C and 60°C. However, the acid-doped zirconia which had been digested at 100°C, remained in the tetragonal phase even after calcination to 900°C. Thus the stabilization of the metastable tetragonal phase is directly related to the digestion at 100°C of the hydrous precursor.

## 3.4. Effect of digestion time on phase formation

The influence of the digestion time on the phase formation was also investigated. After calcination at 500°C, samples B-100-0h-500, B-100-6h-500 and B-100-12h-500 consisted of a mixture of tetragonal and monoclinic phases. Zirconia which had been digested for 24- and 48-h were purely tetragonal while the 96-h sample was x-ray amorphous. Even after treatment to 1000°C, both B-100-48h-1000 and B-100-96h-1000 remained tetragonal (Fig. 3). In contrast, if the precursors had been digested for times shorter than 48 h, increasing amounts of the monoclinic phase were observed after the samples had been

subjected to higher temperatures. Interestingly, after calcining at 1100°C, all samples were predominantly monoclinic ( > 89%). For the 48- and 96-h zirconia, the change is very abrupt from purely tetragonal at 1000°C to mainly monoclinic at 1100°C.

## 3.5. Effect of temperature on surface area

In order to investigate the thermal stability and sintering behaviour, the samples were heated to increasingly higher temperatures. After each heat treatment, they were analyzed by nitrogen adsorption for surface area and by x-ray diffraction for crystallinity, phase structure and particle size. The highest specific surface areas were obtained when the hydrous zirconia samples were calcined at 500°C (Table 1). Upon calcining the samples at progressively higher temperatures, the specific surface areas decreased. The sintering behavior of the different samples is compared in Fig. 4a where the surface area at calcination temperature $T_C$ is normalized to that of the same sample at 500°C. Only undigested and 100°C-digested samples obtained by the acidic, acid-doped and basic preparation methods are shown in the plot. The drop in surface area with calcination temperature $T_C$ appears to be similar all preparations, though for the digested samples, AD-100-48h-$T_C$ and B-100-48h-$T_C$ closely parallel one another. However, in the undigested samples, it is the A-100-48h-$T_C$ and AD-100-48h-$T_C$ series which show comparable surface area loss. The undigested sample which had been aged at 30°C for 48 h, B-30-48h-$T_C$, had a sharp drop in surface area when calcined from 500°C to 600°C and subsequently suffered a smaller loss for 700°C upwards. For the undigested samples from the acid and acid-doped preparation, the decrease in surface area slowed down above 800°C.

The sintering behaviour of the samples which had been digested for different lengths of time at 100°C is shown in Fig. 4b. The plot is again given as the normalized surface area (surface area at $T_C$/surface area at 500°C). For calcination temperatures from 500 to 900°C, the decrease in surface area seems to be independent of the digestion time. Even after heating to 900°C, B-100-96h-900 still has a surface area of 96 m$^2$/g. However, above 900°C, a sharp drop in surface area is observed for samples B-100-48h-$T_C$ and B-100-96h-$T_C$ which have been digested for longer times and which had the highest surface areas at lower temperatures. When the calcination temperature was increased to 1000°C, these samples suffered a dramatic loss in surface area to less than 10 m$^2$/g while samples which had been digested for shorter times (and have a lower surface area) continued with the same sintering trend. The undigested sample also lost surface area though in a less drastic manner than the digested ones.

Between 500 and 900°C, the average crystallite size of the calcined zirconia, as determined from the Scherrer equation, ranges from 5 to 20 nm, depending on the length of time for which the precursors had been digested. As mentioned above, after 1000°C calcination for 12 h, B-100-96h-1000 had lost a tremendous
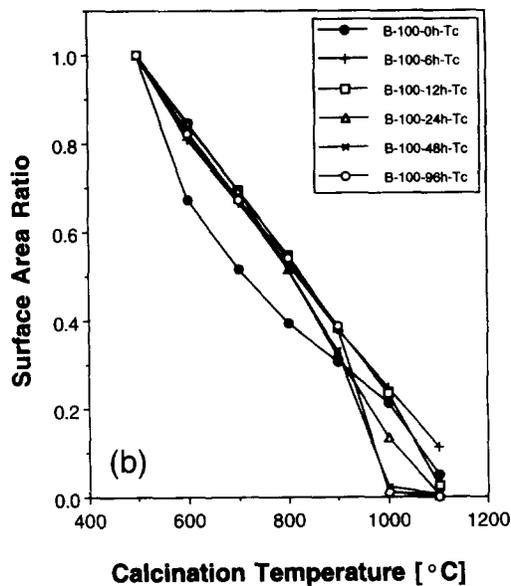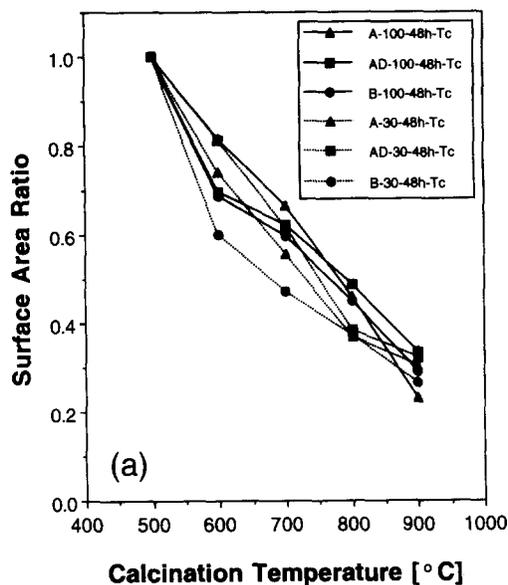
Fig. 4. (a) Relative surface area $(S_T / S_{500°C})$ versus calcination temperature for zirconia prepared using the acidic, basic and lanthanum-doped methods. Dotted lines are for zirconia prepared from precursors which had been aged at 30°C while unbroken lines are from precursors which had been digested at 100°C. (b) Relative surface area $(S_T / S_{500°C})$ versus calcination temperature for zirconia prepared from digestion of the precursor for different lengths of time at 100°C.
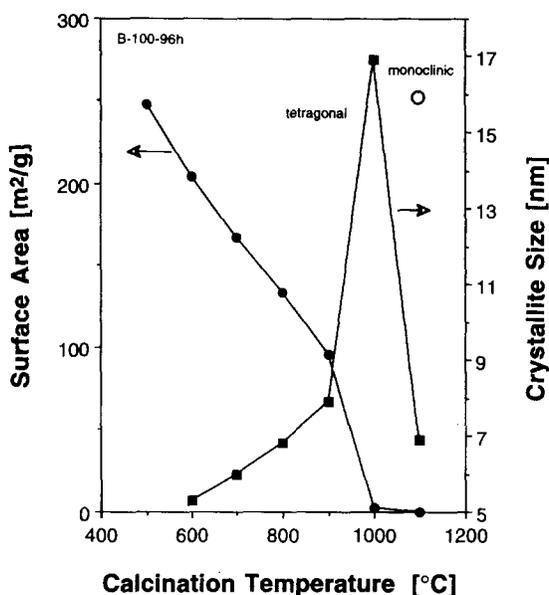
Fig. 5. Crystallite size of the tetragonal and monoclinic phase versus calcination temperature.

amount of surface area. This is accompanied by a considerable increase in the average crystallite size from 7.9 nm in the material heated at 900°C to 17 nm after heating to 1000°C (Fig. 5). Heating the sample to 1100°C led to drastic changes in the microstructure. The tetragonal crystallites present were now much smaller, 6.9 nm, while the monoclinic crystallites made their first appearance with an average size of 16 nm. This suggests that the tetragonal crystallites transform to the monoclinic form once a critical size is reached, whereas the smaller tetragonal crystallites remain in the original structure. Therefore, the average is shifted towards smaller grain size.

From the average crystallite size $D$, percent of each phase and the density for the tetragonal and monoclinic phases (6.10 and 5.85 g/cm$^3$ respectively), an estimate of the surface area can be calculated from the following equation:

$$S = \frac{6 \cdot 10^3}{D\rho} \tag{4}$$

where $\rho$ is expressed in g/cm$^3$, $S$ in m$^2$/g and $D$ in nm. This formula is derived for uniform spherical particles. This relationship between crystallite size and surface area holds for samples with surface area of more than 125 m$^2$/g. However, with increasing calcination temperatures, the loss in surface area is not accompanied by a corresponding growth in the crystallite size. Fig. 6 compares the measured surface area for B-100-96h-$T_C$ with the calculated surface area based on Eq. (4). The two sets of data agree well up to 900°C calcination temperature. However, at 1000°C and 1100°C, the surface area
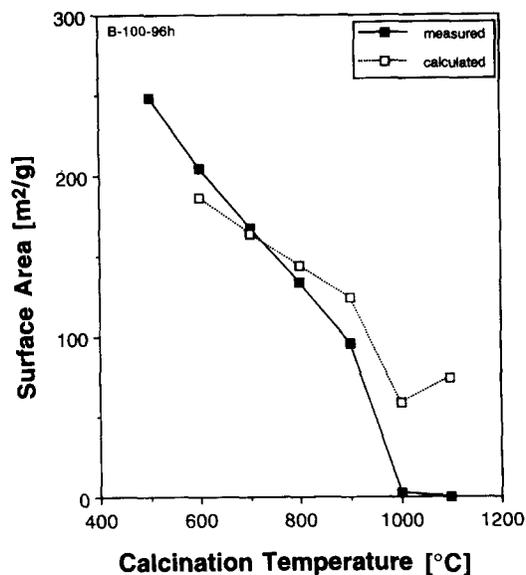
Fig. 6. Comparison of measured BET surface area with the surface area calculated for spherical particles based on the dimensions derived from x-ray line broadening.

calculated from the crystallite size is higher than that measured. Hence, it must be concluded that the observed loss of surface area is mainly due to sintering of individual small particles into bigger, polycrystalline aggregates. The observation that the nanocrystalline structure is conserved during sintering and consolidation of this material may be of interest for the preparation of tough ceramic bodies, as the toughness is inversely related to the grain size by the Griffith equation:

$$\sigma_{\text{fracture}} = \frac{C}{\sqrt{D}} \tag{5}$$

where $C$ is a constant.

## 4. Discussion

High surface area is an important property for use as a support. Many investigators have examined the influence of additives on the structure, thermal stability and texture of zirconia. In this study, we find that small modifications in the preparation greatly influence the ultimate surface area obtainable from the zirconia. The order of addition of the reagents is important. Precipitation effected by adding the zirconium chloride to the ammonium hydroxide gives a significantly higher surface area of the resulting zirconia than vice versa. In the

former case, the precipitation is carried out in a basic media while the reverse involves a pH change in the precipitating solution from 1 to ca. 9.4. It had been found by other workers that doped zirconia shows higher surface area. We found that the surface area can be further improved by digestion of the precursor. The basic series shows very similar surface areas with the acid-doped samples for the same pretreatment; the surface areas are consistently higher than for materials prepared by the acidic method. Hence, digestion provides a convenient route for preparing undoped high surface area zirconia.

Mercera et al. [18] studied the influence of inorganic oxides such as CaO, $Y_2O_3$, MgO and $La_2O_3$ on the thermal stability of monoclinic zirconia. The presence of such oxides, impregnated onto the zirconia, significantly improved the resistance to thermal sintering. The authors observed by transmission electron microscopy that at higher calcination temperatures, crystallite growth occurred together with inter-crystallite sintering via neck-formation and growth. At temperatures less than $1/2$ $T_m$ (Tamman temperature), the mass transport necessary for the sintering process is largely by surface diffusion. The additives inhibit surface diffusion and thereby reduce sintering. Norman et al. [16] studied the role of the anions, sulphate and carbonate, on the surface area stabilization of zirconia and found that the presence of sulphate hinders sintering. Their explanation for this stabilization of surface area was based on the presence of sulphate bridges which increases the zirconium–zirconium separation from 0.33–0.37 nm for hydroxo bridges to 0.35–0.43 nm for sulphate bridges. The longer distance between zirconium is believed to delay the nucleation and crystallization.

The hydrous zirconia originally precipitates as a gel, the washing of which posed some difficulties. This led us to digest the gel-like precipitates in order to obtain more crystalline precipitates. The temperature of digestion was found to influence the surface area of the zirconia with 100°C being the most effective. By digesting the hydrous zirconia at 100°C, a three- to five-fold increase in the surface area is obtained in the zirconia from the acidic, acid-doped and basic series when compared to the undigested samples.

In order to explain the effects of digestion on the surface area and crystal phase of zirconia that is formed after calcination of the precursor, we propose that during digestion, the structure of the hydrous oxide precursor changes. In our experiments using ammonium hydroxide as the precipitating agent, we observed that the hydrous oxide after drying in the oven at 100°C was x-ray amorphous. Other workers, however, have shown that the crystal structure of the gel-like precipitate which formed on addition of zirconium chloride to ammonium hydroxide or vice versa is different depending on the temperature [20,21]. Thermodynamic analysis of the $ZrO_2$–$H_2O$ system by Adair et al. [22] showed that zirconium hydroxide, $Zr(OH)_xO_y$, is the stable solid phase below about 85°C. Above this temperature, monoclinic zirconia, $ZrO_2$, becomes thermodynamically stable. Powers and Gray [23] demonstrated that dimerization of

Zr(OH)$_4$ by elimination of water from the double hydroxo groups to form oxo bridges occurs above 80°C. The increase in the digestion temperature brings about changes in the structure of the hydrous zirconia precursor and leads to a more dehydrated oxo-hydroxide. Our experiments clearly show that digestion at $T_D > 80$°C resulted in greatly enhanced surface area of the resulting zirconia. We propose that upon calcination, the more dehydrated oxo-hydroxide which formed above 80°C decomposes to give very fine crystallites of zirconia. This results in the high surface area. Another observation made in our experiments was that longer digestion times at 100°C also brought about an increase in the surface area. Obviously the transition to dehydrated oxo-hydroxide is very sluggish so that a longer digestion time results in a bigger loss of water from the hydrous oxide. The higher fraction of dehydrated oxo-hydroxide in turn leads to the high surface zirconia after calcination. Clearfield [24,25] found that refluxing transformed the amorphous gel particles into a crystalline product, which he identified as the hydrated oxo-hydroxide, $[ZrO_x(OH)_{4-2x} \cdot yH_2O]_n$. The initially precipitated hydrous oxide differs from the crystalline product in that it has a much smaller value of $x$ and also contains some foreign atoms. Refluxing of the base-precipitated, gelatinous hydrous oxide results in an increase in $x$ and a decrease in the foreign anion content.

With respect to the acidic preparation, it is found that the presence of lanthanum ions stabilizes the tetragonal phase irrespective of the temperature of digestion. This holds true for zirconia calcined at 500°C and 600°C. However, after calcination at 700°C, zirconia from lanthanum-doped hydrous oxides which have been aged at 30°C or digested at 60°C was partly monoclinic. Only samples digested at 100°C remained purely tetragonal up to 900°C. The stabilization of the tetragonal phase in doped zirconia has been observed by others [1,8] and it is postulated that the incorporation of lanthanum cations in solid solution substantially decreases the specific surface free energy of zirconia. This favours the tetragonal modification in the lanthanum-doped zirconia as the tetragonal phase was reported by Garvie [26,27] and by Garvie and Goss [28] to have a lower surface free energy than the monoclinic form.

We observed in our experiments the interesting effect digestion has on the formation and stability of the tetragonal phase in the *undoped* samples even to very high calcination temperatures. Samples digested at 80°C or higher show a marked increase in the tetragonal phase. In fact, the 100°C-digested samples of the undoped acid and basic series yielded pure tetragonal zirconia even when calcined up to 900°C. It should be noted that digestion at 100°C is not a sufficient condition for obtaining stabilized tetragonal zirconia. The stabilization is also dependent on the length of time during which the hydrous oxide has been digested. Hydrous oxides digested for 48 h or longer maintain the tetragonal form to 1000°C and converted to the monoclinic form only at 1100°C. The transition was very sharp and after calcination at 1100°C, the zirconia consisted of more than 90% monoclinic phase. In contrast, samples which had also been

digested at 100°C but for shorter times, show a gradual increase in the amount of monoclinic phase with calcination temperature.

As mentioned earlier, digestion above 80°C results in a more dehydrated oxo-hydroxide precursor. Obviously, the crystal phase obtained in the calcined product depends on the oxo-hydroxide precursor formed during digestion. Our results indicate that calcination of this dehydrated oxo-hydroxide gives the tetragonal phase while the more hydrated precursor leads to the monoclinic structure. It is possible that the crystallite size of the dehydrated oxo-hydroxide precursor is finer than that of the more hydrated form. In this case, the specific surface energy may favour the tetragonal structure in the precursor [26–28]. Calcination of the tetragonal precursor might then result in the corresponding tetragonal zirconia. Srinivasan et al. [29] concluded from TGA and DSC measurements that monoclinic and metastable tetragonal zirconia are formed from the corresponding x-ray amorphous monoclinic and tetragonal hydrous zirconia and not from a common precursor.

The stabilization of the metastable tetragonal phase up to 1000°C in the longer digested samples may be due to the effects of digestion on the purity of the sample. Digestion leads to a purer solid due to the dissolution and recrystal-lization that occur continuously during this digestion process. The rate of dissolution and recrystallization is increased with the digestion temperature. Contaminants which are incorporated within the interior of the crystals during precipitation by inclusion or occlusion can escape from the solid. Hence, the crystals grow to perfection with little defect sites. During calcination, a topotac-tic transformation of the precursor to zirconia takes place [21]. In pure undoped zirconia, Schottky defects are the most frequently occurring defects [13]. A Schottky defect consists of a missing cation and a missing anion of equal charge, in this case for every zirconium vacancy there will be two oxygen vacancies. The number of non-equilibrium defects decreases with time and temperature of digestion. In the calcined samples, once the metastable tetragonal phase has formed, it can withstand high temperatures due to its small crystallite size. The conversion from tetragonal to monoclinic is hindered because there are not enough defect sites for mass transport to take place. Indeed, the tetragonal state is observed to 1000°C, a much higher temperatures than has been previ-ously reported. Samples which have been digested for shorter times or at lower temperatures have more defect sites. Therefore, the rate of bulk and surface diffusion will be enhanced. This leads to crystallite growth. Once the crystallites reach a critical size, the free energy for transformation to the monoclinic phase becomes negative and monoclinic structure forms. High lattice mobility will also facilitate the ion movement necessary for this transition from tetragonal to monoclinic.

## 5. Conclusion

(1) The precipitation of hydrous zirconia in a basic medium produces a precursor which can be converted into zirconia with higher surface area than that obtainable from material which was precipitated at low pH.

(2) Digestion of the hydrous zirconia above 80°C increases the surface area of the calcined zirconia by as much as five-fold. The zirconia obtained had similar surface areas to lanthanum-doped zirconia. Hence, this is a useful method for preparing high surface area zirconia without the need to incorporate other oxides.

(3) The time and temperature of digestion and the pH of the digestion medium are important factors which determine the surface area of zirconia.

(4) By digesting samples at 100°C for longer than 24 h, pure tetragonal phase zirconia which has high thermal stability can be obtained. This material converts into the monoclinic modification only after heat treatment to 1100°C.

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## References

[1] T. Yamaguchi, Catal. Today, 20 (1994) 199.
[2] M. Ye and J.G. Eckerdt, J. Catal., 87 (1984) 381.
[3] W.B. Johnson and J.G. Eckerdt, J. Catal., 126 (1990) 146.
[4] K. Domen, J. Kondo, K. Maruya and T. Onishi, Catal. Lett., 12 (1992) 127.
[5] Y. Nakano, T. Yamaguchi and K. Tanabe, J. Catal., 80 (183) 307.
[6] J.W. Joyner, Zirconium in Catalysis, A Review of Current Scientific Literature, Report by Magnesium Electron Chemicals Division.
[7] F.R. Chen, G. Coudurier, J.-F. Joly and J.C. Vedrine, J. Catal., 143 (1993) 616.
[8] T. Yamaguchi, Appl. Catal., 61 (1990) 1.
[9] M. Ozawa and M. Kimura, J. Mater. Sci. Lett., 9 (1990) 446.
[10] M. Inoue, H. Kominami and T. Inui, Appl. Catal. A, 97 (1993) L25.
[11] B. Aiken, W.P. Hsu and E. Matijević, J. Mater. Sci., 25 (1990) 1886.
[12] A. Garg and E. Matijević, J. Colloid Interface Sci., 126 (1988) 243.
[13] P.D.L. Mercera, J.G. Van Ommen, E.B.M. Doesburg, A.J. Burggraaf and J.R.H. Ross, Appl. Catal., 57 (1990) 127.
[14] P.D.L. Mercera, J.G. Van Ommen, E.B.M. Doesburg, A.J. Burggraaf and J.R.H. Ross, Appl. Catal., 78 (1991) 79.
[15] R. Srinivasan, D. Taulbee and B.H. Davis, Catal. Lett., 9 (1991) 1.
[16] C.J. Norman, P.A. Goulding and I. McAlpine, Catal. Today, 20 (1994) 313.
[17] B. Fegley, Jr., P. White and H.K. Bowen, Am. Ceram. Soc. Bull., 64 (1985) 1115.
[18] P.D.L. Mercera, J.G. Van Ommen, E.B.M. Doesburg, A.J. Burggraaf and J.R.H. Ross, Appl. Catal., 71 (1991) 363.
[19] K.S. Chan, G.K. Chuah and S. Jaenicke, J. Mater. Sci. Letts., 13 (1994) 1579.

[20] J.H. Adair and R.P. Denkewicz, Ceram. Trans., 12 (1990) 25.
[21] R.P. Denkewicz, Jr., K.S. TenHuisen and J.H. Adair, J. Mater. Res., 5 (1990) 2698.
[22] J.H. Adair, R.P. Denkewicz and F.J. Arriagada, Ceram. Trans., 1 (1988) 135.
[23] D.A. Powers and H.B. Gray, Inorg. Chem., 12 (1973) 2721.
[24] A. Clearfield, Rev. Pure Appl. Chem., 14 (1964) 91.
[25] A. Clearfield, G.P.D. Serette and A.H. Khazi-Syed, Catal. Today, 20 (1994) 295.
[26] R.C. Garvie, J. Phys. Chem., 69 (1965) 1238.
[27] R.C. Garvie, J. Phys. Chem., 82 (1978) 218.
[28] R.C. Garvie and M.F. Goss, J. Mater. Sci., 21 (1986) 1253.
[29] R. Srinivasan, M.B. Harris, S.F. Simpson, R.J. De Angelis and B.H. Davis, J. Mater. Res., 3 (1988) 787