

Stabilized tetragonal zirconium oxide as a support for catalysts

Evolution of the texture and structure on calcination in static air

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Abstract

Single-phase tetragonal zirconium oxides have been made by the incorporation of 5.4 mol-% of Y^{3+} or La^{3+} in ZrO_2 to form solid solutions. The samples were prepared by controlled coprecipitation from aqueous solutions of the respective metal chlorides at room temperature and at a constant pH of 10, followed by calcination at 500°C (in the case of the Y^{3+} -doped sample) or 600°C (in the case of the La^{3+} -doped sample) to effectuate the crystallization into the tetragonal phase. The process of crystallization of the hydrous zirconia precursor was found to be retarded by the incorporation of Y^{3+} or La^{3+} , the latter giving the greater effect. Upon crystallization, stabilized tetragonal samples were obtained with high specific surface areas (S_{BET} ca. 88 m² g⁻¹ for both the samples) and well-developed mesoporous textures but without any microporosity. Both the Y^{3+} - and the La^{3+} -alloyed ZrO_2 samples were found to fully retain the tetragonal phase upon calcination over the entire range of temperatures studied (up to 900°C). The thermal stability of the texture of zirconia was found to be considerably improved, in comparison with the undoped monoclinic material, by the stabilization of the crystal structure in the defect tetragonal form. In particular, incorporation of 5.4 mol-% of La^{3+} resulted in a support material which had a remarkable thermal stability. It is shown that the improvements in the thermal stability are derived from a strong inhibition of the processes of crystallite growth and the accompanying inter-crystallite sintering and thus of the process of mass transport; the mass transport probably occurs by a mechanism of surface diffusion.

Keywords: stabilized tetragonal zirconia, structural and textural stabilizers (Y^{3+} and La^{3+}), preparation (coprecipitation), thermal stability, catalyst characterization (TG, DTA, TEM, XRD, and N_2 -physorption).

INTRODUCTION

Most heterogeneous catalysts, apart from those based on zeolites, are composed of a support and an active phase. Many industrial applications require

supports which combine a high specific surface area with good thermal and chemical stabilities, even in the presence of water vapour. Additionally, the internal surface area of the support must be easily accessible to the reactants, a requirement which implies that the pores must not be too narrow (The most frequent pore radius must preferably be larger than 50 Å [1].)

In recent years, interest in the use of catalyst supports other than alumina, silica and silica-alumina has increased and research efforts are currently being directed towards the development of new support materials based on oxides such as titania [2], magnesia [3], ceria [4], lanthana [5] and zirconia [6-8]. Our laboratory is currently involved in a research programme aimed at (i) the development and characterization of high-surface-area zirconium dioxides with well-developed mesoporous textures which are stable under thermal and hydrothermal conditions and (ii) the investigation of possible (new) applications of zirconia as a support. Generally, the interest in zirconia as a support material can be ascribed to at least one of the following three properties: (i) as a carrier, it gives rise to a unique kind of interaction between the active phase and support, this being manifested in both the catalytic activity and the selectivity pattern of the system [9,10]; (ii) it can be more chemically inert than the classical supports (e.g. γ -alumina or silica) [11,12]; and (iii) it is the only single-metal oxide which may possess four chemical properties, namely acidity or basicity as well as reducing or oxidizing ability [6].

Zirconia exhibits three well-established polymorphs, the monoclinic, tetragonal and cubic phases [13]. The monoclinic phase is stable up to 1170°C, at which temperature it transforms into the tetragonal phase, which is stable up to 2370°C. This high-temperature tetragonal phase cannot be retained upon rapid cooling to room temperature, i.e. it cannot be quenched [14]; however, it can be obtained in a metastable condition at much lower temperatures if the zirconia is prepared either by precipitation from (aqueous) solutions or by thermal decomposition of zirconium salts [15-17]. Above 2370°C, the cubic phase is stable and it exists up to the melting point of 2680°C; this high-temperature cubic phase can also not be quenched [14]. The structures of the tetragonal and the cubic phases of zirconia can however be stabilized at room temperature by the incorporation of many different metal cations, among which are Mg^{2+} , Ca^{2+} , Sc^{3+} , Y^{3+} , La^{3+} and Ce^{4+} , to form solid solutions [18] (materials commonly referred to as stabilized tetragonal or cubic zirconium oxides); the amount of dopant required for the stabilization of either of the modifications depends upon the nature of the dopant and, most importantly, upon the method of preparation. (Equilibrium studies over extended times have shown in many cases (e.g. in the cases of Y^{3+} and La^{3+}) that neither the stabilized tetragonal nor the stabilized cubic phases of zirconia are truly stable at room temperature [19,20]. The low rate of the destabilization process is due to the very low cation diffusion coefficients. As a consequence, the fluorite-like

phases remain metastable for long periods of time at temperatures well below the normal phase transition temperatures.)

In previous papers [7,8,17], we have shown that metastable tetragonal and single-phase monoclinic zirconia samples with high specific surface areas and with well-developed mesoporous textures could be made by means of gel-precipitation, followed by calcination at 450°C; the preparation techniques used to produce either of the modifications differed only in the nature of the washing media employed, the promoting effect of ethanol-washing on the phase transition metastable tetragonal to monoclinic zirconia [17] being exploited to yield the single-phase monoclinic sample. However, neither of these polymorphs was found to have stable porous textures upon calcination in air at higher temperatures: both the high specific surface areas and the pore volumes decreased markedly with increase of temperature up to 900°C. The thermal stability of monoclinic zirconia was found to be improved significantly by the addition (by an impregnation technique) of oxides such as CaO, Y₂O₃ or La₂O₃. The best results were obtained with La₂O₃. However, the effectiveness of these additives as sintering inhibitors was found to decrease with increase in calcination temperature, the decrease in effectiveness being much more dramatic in the cases of the CaO- and Y₂O₃-doped samples than in the case of the La₂O₃-doped ones. Generally, three processes were identified as being responsible for the changes in the pore structure and surface area occurring on calcination: (i) phase transformation (from the metastable tetragonal structure into the monoclinic modification or, in the cases of the impregnated samples, from the monoclinic structure into a fluorite-like phase); (ii) crystallite growth and the accompanying inter-crystallite sintering; and (iii) agglomeration. Since the occurrence of an appreciable degree of phase transformation is likely to be detrimental to both the textural stability and the mechanical properties of the zirconia support material, there being a large volume change (3–5%) associated with the process of phase transformation, we have now carried out a series of experiments with the aim of examining the effect of additives which give rise to the so-called 'stabilized tetragonal zirconias' on the textural development of such materials on heating.

From the work of, among others, Bastide et al. [20], Theunissen [21], Boutz et al. [22] and Silver et al. [23], it is known that the process of crystallite growth is strongly inhibited by stabilizing the structure of the zirconia into the defect tetragonal modification by alloying it with cations such as Y³⁺, La³⁺ or Ce⁴⁺. From the published non-equilibrium data for the binary systems Y₂O₃-ZrO₂ [21–24], La₂O₃-ZrO₂ [20,25,26] and CeO₂-ZrO₂ [21,22,27], it can be concluded that Y³⁺ and La³⁺ are the better structural stabilizers, these two additives requiring the lowest concentrations (3.9 mol-%) to fully stabilize the tetragonal phase of zirconia; for Ce⁴⁺, a minimum of 9 mol-% is required to render the tetragonal modification stable. As preliminary experiments performed by us showed that 3.9 mol-% of La³⁺ was insufficient to retain all of

the tetragonal phase after sintering in static air for 15 h at 900°C, some monoclinic phase being detected in the X-ray diffractogram of this sample, we have chosen to prepare the stabilized tetragonal zirconium oxides by alloying zirconia with 5.8 mol-% of Y^{3+} or La^{3+} . Moreover, Silver et al. [23] have shown that the specific BET surface area of yttria-stabilized zirconia was not improved further by the incorporation of more than 5.8 to 7.7 mol-% of Y^{3+} .

Because of their importance as 'technical ceramic materials', extensive studies have been made of the structural, mechanical and electrical properties of stabilized zirconium oxides (both tetragonal and cubic). On the other hand, the textural properties of these materials have not been examined as closely; in fact, whereas a few (systematic) studies of the development of the porous texture of yttria-stabilized zirconia upon heat treatment have been made [23,28,29], to the best of our knowledge no such studies have been conducted on lanthana-stabilized zirconium oxide, although the work reported by Turlier et al. [30], who studied the textural stabilization of non-porous metastable tetragonal zirconia by the addition (by an impregnation technique) of yttria or lanthana, can be considered as a close precedent to the present investigation. This paper thus describes: (i) a synthesis route which affords high-surface-area stabilized tetragonal zirconium oxides; and (ii) the results of a systematic study of the stability of the porous texture of an yttria- and a lanthana-stabilized tetragonal zirconium oxide after calcination in static air at various temperatures up to 900°C.

EXPERIMENTAL

Preparation of the samples

Samples of hydrogel were made by controlled coprecipitation at room temperature. The starting materials were high-purity salts of $ZrOCl_2 \cdot 8H_2O$, $LaCl_3 \cdot 7H_2O$ and $YCl_3 \cdot 6H_2O$ (all Merck, Pro Analysis). Solutions (0.41 M total cation concentration) (i) of zirconyl and lanthanum chloride (corresponding to 5.8 mol-% La^{3+} in the final oxide) and (ii) of zirconyl and yttrium chloride (corresponding to 5.8 mol-% Y^{3+} in the final oxide) were prepared by slowly adding the salts to constantly stirred doubly distilled water. Each mixed chloride solution was then added dropwise, at a rate of $10 \text{ cm}^3 \text{ min}^{-1}$, concurrently with a solution of ammonia (Merck, Pro Analysis, 6.7 M) to doubly distilled water, the pH of which had been adjusted to 10 with ammonia; the pH was maintained at 10 by adjusting the rate of addition of the ammonia solution. The whitish gelatinous precipitate formed was aged in the mother liquor for 65 h; after filtration, it was washed in a sequence of repeated steps involving redispersion in doubly distilled water and filtration until the wash-water gave a negative test for chloride ions (silver nitrate test). The chloride-free hydrogel was then subjected to two cycles involving redispersion in ethanol (purity

99.8%) followed by filtration. The precipitation and washing steps were carried out in the reactor described previously [7]. After the last dispersion/filtration step, the hydrous zirconia was dried in static air at 110°C for 20 h and then dry-milled in a plastic container employing teflon balls to yield a fluffy white powder. The samples doped with Y^{3+} or La^{3+} were designated ZrY3 and ZrLa3, respectively.

Chemical analysis

The purity of the samples ZrY3 and ZrLa3 and the quantities of Y^{3+} and La^{3+} incorporated were determined using X-ray fluorescence analysis (XRF, Philips PW 1410 spectrometer). The bulk chloride content, which serves as a quality control parameter, was determined quantitatively by an argentometric method, the details of which were given previously [7].

Sintering experiments

The samples were studied both in the freshly prepared state and after sintering. Sintering studies were performed by treating the samples at various temperatures up to 900°C in static air in a tube furnace; the temperature was increased at a rate of 3°C min⁻¹ to the final temperature, this being maintained for 15 h before the sample was cooled to 200°C at a rate of 5°C min⁻¹, after which it was cooled rapidly to room temperature.

Characterization techniques

The samples were characterized by thermogravimetry (TG), differential thermal analysis (DTA), nitrogen physisorption measurements, transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). The thermal analysis were performed in a flow of air (35 cm³ min⁻¹) using an apparatus which simultaneously recorded the TG and DTA signals (PL Thermal Sciences, STA-1500). The experiments were all performed by raising the temperature linearly at a rate of 10°C min⁻¹ and the sample size ranged from 18.0 to 18.5 mg. A sample of α -Al₂O₃ (17.2 ± 0.2 mg) was used as reference for the DTA measurements.

Full nitrogen adsorption-desorption isotherms at -196°C were obtained using a Micromeritics ASAP 2400 system. Prior to the physisorption measurements, all the samples were outgassed for 6 h at 300°C. Analysis of the isotherms was carried out as described previously [7].

Transmission electron microscopy was carried out using a JEOL 200CX Electron Microscope operated at 200 kV. TEM specimens were prepared by ultrasonically dispersing the powder samples in ethanol (Merck, Pro Analy-

sis) and then applying drops of this suspension to a carbon film supported on a copper grid.

X-ray diffraction patterns were recorded using a Philips PW 1710 diffractometer with nickel-filtered Cu K α radiation. Both continuous and step-scan techniques were used, the former being employed for phase identification and the latter for quantitative analysis. The step-scans were taken over the range of 2θ from 26 to 33° in steps of 0.015° (2θ), the intensity data for each point being collected for 10 s. In order to further improve counting statistics, rotation about the normal axis was used. The crystallite sizes (D_{111}) of the various samples were calculated for the (111) reflection of the tetragonal phase by using the Scherrer relationship (eqn. 1):

$$D_{111} = \frac{0.9\lambda}{B_{111}\cos\theta} \quad (1)$$

B_{111} , the width of the peak at half the peak maximum corrected for the effects of spectral and instrumental broadening, was determined as described previously [7].

RESULTS AND DISCUSSION

Chemical analysis

XRF analyses of the samples ZrY3 and ZrLa3 revealed the presence of the following impurities: Hf (major impurity), traces of Cu, Fe, Ti, K and Si, together with some Cl. The bulk chloride analyses showed that the two samples contained less than 50 ppm of chloride ions (50 ppm is approximately the detection limit of the method employed). The contents of Y³⁺ and La³⁺ in ZrY3 and ZrLa3 respectively (after calcination for 15 h at 800°C in air) were both found to be 5.4 mol-%. The analyzed quantities are in reasonable agreement with the nominal starting compositions.

Freshly prepared samples: thermal analysis and crystallization

The X-ray diffractograms of the uncalcined samples showed only two very broad bands in the range of 2θ from 18 to 40° and from 40 to 70°, this being indicative of a very low degree of crystallinity. The lack of well-defined reflections in the XRD patterns of the xerogels is typical for zirconia prepared via wet-chemical routes [7].

Typical TG and DTA results of the decomposition of the dried gels, ZrY3 and ZrLa3, are shown in Figs. 1 and 2, respectively. The TG weight loss curves (Figs. 1a and b) are typical of those found with a hydrous zirconia which had been dehydrated with an alcohol prior to the drying step [17,31]. For both the samples, the weight loss occurred in four distinct stages, the DTG-traces show-

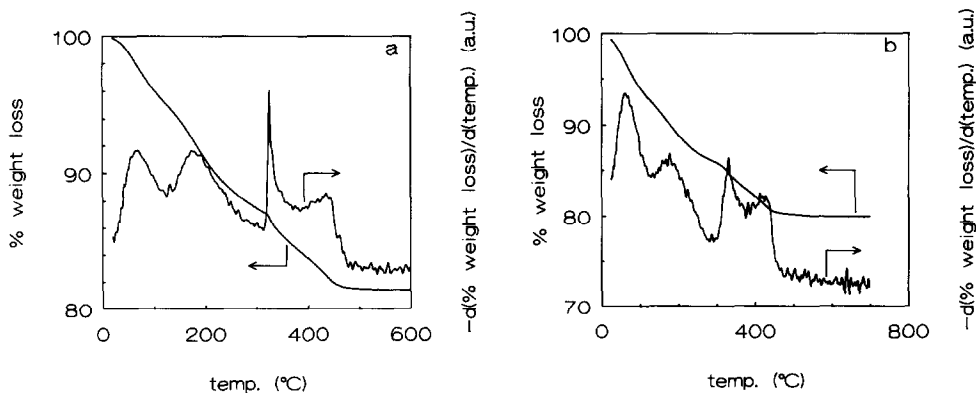


Fig. 1. Typical thermogravimetric analysis (TG) results of the decomposition of the xerogels (a) ZrY3 and (b) ZrLa3.

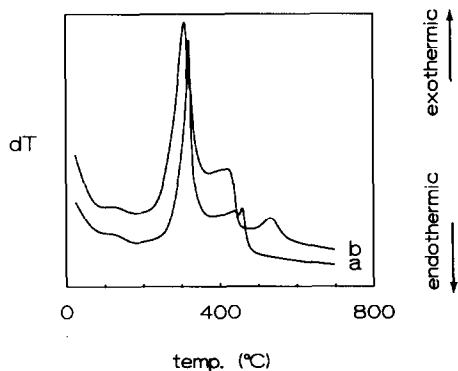


Fig. 2. Typical differential thermal analysis (DTA) results of the decomposition of the xerogels ZrY3 (trace a) and ZrLa3 (trace b).

ing maxima at about 65, 181, 324 and 430°C. The first two stages correspond to the desorption of physically adsorbed water and the volatilization of water of crystallization respectively. The third and fourth peak in the DTG-traces correspond to the oxidative decomposition of chemisorbed ethanolic species (i.e. surface ethoxy groups), a process which is likely to be ZrO_2 -catalyzed [17,31]. The loss of weight was complete at about 470°C and was equivalent to about 20% of the initial sample weight. As shown in Fig. 2, the first two weight losses were mildly endothermic while the third and the fourth were exothermic (exotherms at about 313 and 430°C respectively). The so-called 'glow exotherm', characteristic of the crystallization of the initially (X-ray) amorphous hydrous zirconia [7,17], was only clearly distinguishable for the ZrLa3 sample as a broad exothermic peak centered around 534°C (Fig. 2, trace b). However, as shown in Fig. 3 (a and b), crystallization exotherms were

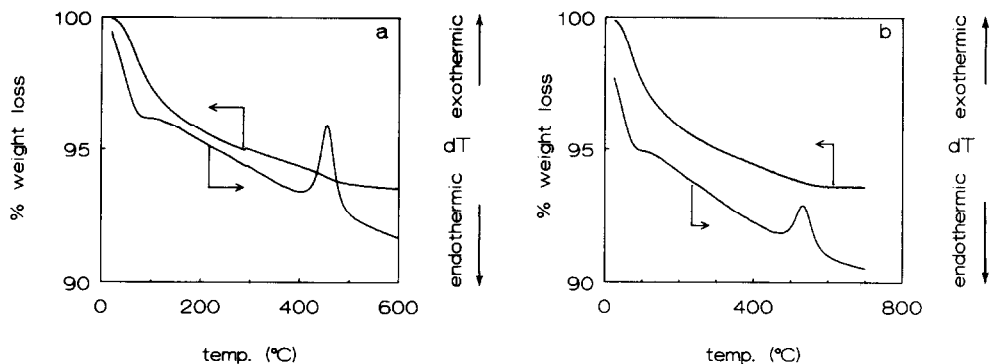


Fig. 3. TG and DTA results on (a) ZrY₃ and (b) ZrLa₃, both calcined in flowing air for 15 h at 350°C prior to the thermal analyses measurements.

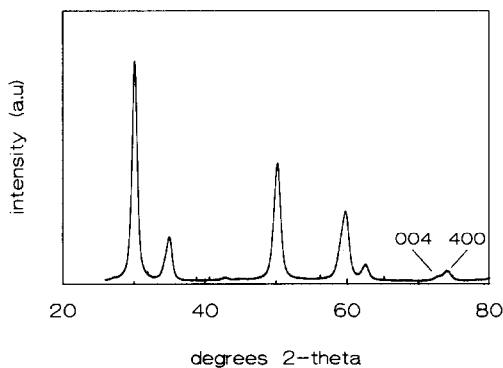


Fig. 4. Typical X-ray powder diffractogram on ZrLa₃ calcined for 15 h at 600°C.

clearly discernable in the DTA results for the samples ZrY₃ and ZrLa₃ which had been calcined in flowing air ($150 \text{ cm}^3 \text{ min}^{-1}$) for 15 h at 350°C prior to the TG/DTA experiments; both these samples were (still) amorphous to X-rays. The exotherm for ZrY₃ occurred at about 454°C (Fig. 3a) while that for ZrLa₃ occurred at about 534°C (Fig. 3b), the same temperature as in Fig. 2 (trace b). The glow exotherm was accompanied by a small weight loss (TG curves of Figs. 3a and b), probably due to a continued loss of water (by combination of surface hydroxyl groups) and of CO_x (products of the combustion of the ethanolic species). The glow exotherm of an undoped hydrous zirconia prepared by an analogous route, i.e. the hydrous precursor to the monoclinic samples ZC5-10E described in [8], occurred at about 438°C.

A typical X-ray powder diffraction pattern of the sample ZrLa₃ calcined at 600°C is presented in Fig. 4; the diffractogram of the sample ZrY₃ crystallized at 500°C was almost identical. The patterns were characteristic of tetragonal zirconia, the (004) and (400) reflections of the tetragonal phase being readily

TABLE 1

X-ray lattice spacings for the (111), (222) and (400) reflections of the tetragonal phase for ZrY3, ZrLa3 and two undoped metastable tetragonal zirconia (*t*-ZrO₂) samples

Sample	d_{111} (Å)	d_{222} (Å)	d_{400} (Å)
ZrY3 ^a	2.960	1.48	1.28
ZrLa3 ^b	2.971	1.485	1.28
undoped metastable <i>t</i> -ZrO ₂ ^c	2.950	1.47	1.27
undoped metastable <i>t</i> -ZrO ₂ ^d	2.949	1.474	1.270

^aSample ZrY3 calcined for 15 h at 500°C.

^bSample ZrLa3 calcined for 15 h at 600°C.

^cUndoped metastable tetragonal zirconia sample prepared in our laboratory by gel-precipitation followed by freeze-drying and calcination in flowing air (150 cm³ min⁻¹) for 15 h at 450°C [32].

^dASTM powder diffraction index, file no. 14-534.

discernable and, more important, deconvolution of the reflections over the range of 2θ from 72 to 76° giving no evidence of the cubic phase. Table 1 gives the lattice spacings (d_{hkl}) calculated from these X-ray diffractograms for the tetragonal (111), (222) and (400) reflections of ZrY3 and ZrLa3 (calcined for 15 h at 500 and 600°C respectively). For comparison purposes, the lattice spacings of two undoped metastable tetragonal zirconia samples are also given, one of these having been prepared in our laboratory [32] and the other being an ASTM standard. The lattice spacings for both ZrY3 and ZrLa3 are somewhat greater than those found for undoped metastable tetragonal zirconia, this being indicative of the formation of solid solutions. Furthermore, the lattice spacings for ZrLa3 were somewhat higher than those of ZrY3; this is consistent with the effective cationic radii, that for La³⁺ (1.16 Å) being larger than that of Y³⁺ (1.02 Å).

It is thus clear that the incorporation of 5.4 mol-% of Y³⁺ or La³⁺ in ZrO₂ gives rise to solid solutions and results in: (i) a retardation of the process of crystallization of hydrous zirconia, La³⁺ showing the greatest retarding effect; and (ii) single-phase tetragonal zirconia upon crystallization. These results are in good agreement with the findings of other investigators [20,33–36] for similar binary zirconia systems involving incorporation of Y³⁺ or La³⁺.

Development of the texture of ZrY3 and ZrLa3 upon sintering in static air

Large batches of the dried gels ZrY3 and ZrLa3 were calcined in static air for 15 h at 500 and 600°C, respectively, to bring about crystallization and to provide the starting materials for the sinter experiments. Full nitrogen ad-

sorption-desorption isotherms were measured for granules of the as-calcined materials; to this end, portions of the powder samples were pressed at 592 MPa, crushed and sieved to a particle size of 0.3–0.6 mm. The isotherm obtained with ZrLa3 is shown in Fig. 5; the isotherm obtained with ZrY3 was almost identical. Both the isotherms were of type IV (BDDT classification [37,38]), being characteristic of well-developed mesoporous systems (pore radii between 10 and 250 Å [38]); the shapes of the hysteresis loops resembled that of type A (following the classification of De Boer [39]) and were characteristic of agglomerates of spheroidal particles of fairly uniform size and inter-particle coordination number [37,38]. The most important textural parameters calculated from the isotherms are listed in Table 2. The values of S_{BET} were calculated by the BET method by assuming a value of 0.162 nm² for the cross-sectional area of the nitrogen molecule [38] while the values of S_t (the sum of the area of the mesopore walls and the external surface) were determined using the t -plot method [40]. The pore volumes, V_p , were calculated from the pla-

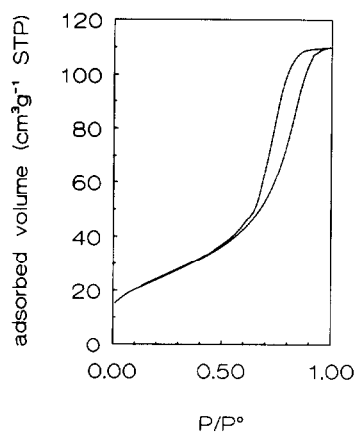


Fig. 5. A representative nitrogen adsorption-desorption isotherm at -196°C obtained with granules of the sample ZrLa3 which has been calcined at 600°C .

TABLE 2

Physical properties of ZrY3 and ZrLa3 after calcination at 500 and 600°C , respectively

Sample	Phase	S_{BET} (m^2g^{-1})	S_t (m^2g^{-1})	V_p (cm^3g^{-1})	$R_p(\text{ads})$ (Å)	$R_p(\text{des})$ (Å)	D_{J11} (Å)
ZrY3	100% tetragonal	88	89	0.16	52	36	121
ZrLa3	100% tetragonal	87	90	0.17	54	37	122

teaus of the adsorption isotherms [37]. The values of the most frequent pore radii R_p (ads) and R_p (des) were calculated following the BJH method and assuming cylindrical pore model [7,41], the calculations being applied to either the adsorption (R_p (ads)) or desorption (R_p (des)) branches of the isotherms. From the results summarized in Table 2, it is clear that the samples had well-developed mesoporous textures; furthermore, the good agreement between the S_{BET} and S_t values indicates [7] that the samples were free of micropores (pores with radii not exceeding about 10 Å [38]).

Typical TEM micrographs of the as-calcined powder samples are shown in Fig. 6; micrograph 6a showing the morphology of ZrY3 (calcined at 500°C), and micrograph 6b that of ZrLa3 (calcined at 600°C); each sample consisted of reasonably uniform, rounded crystallites which were agglomerated. The par-

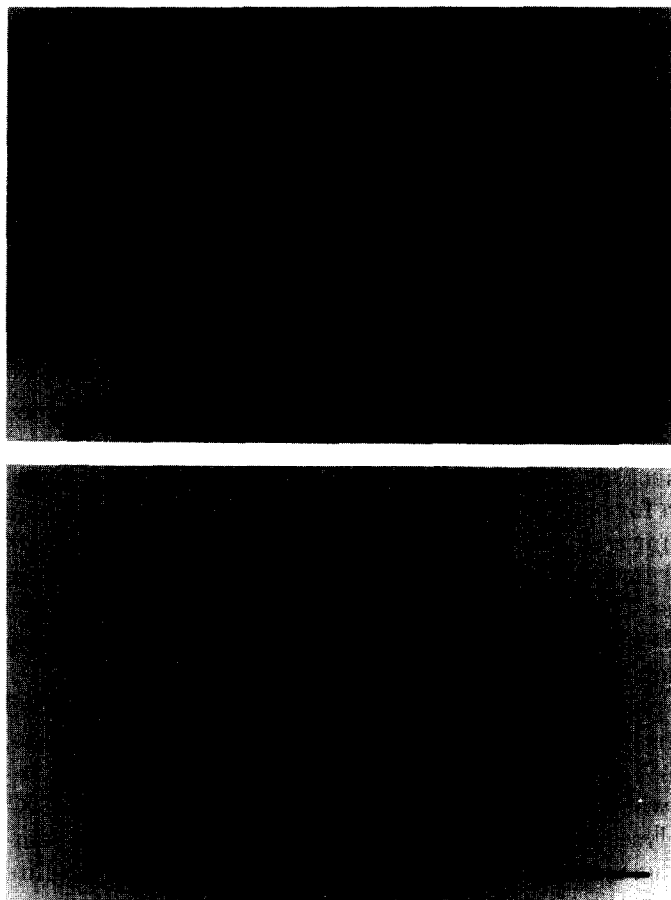


Fig. 6. Typical transmission electron micrographs of the samples (a) ZrY3 calcined at 500°C and (b) ZrLa3 calcined at 600°C. The bar indicates a measurement of 100 nm.

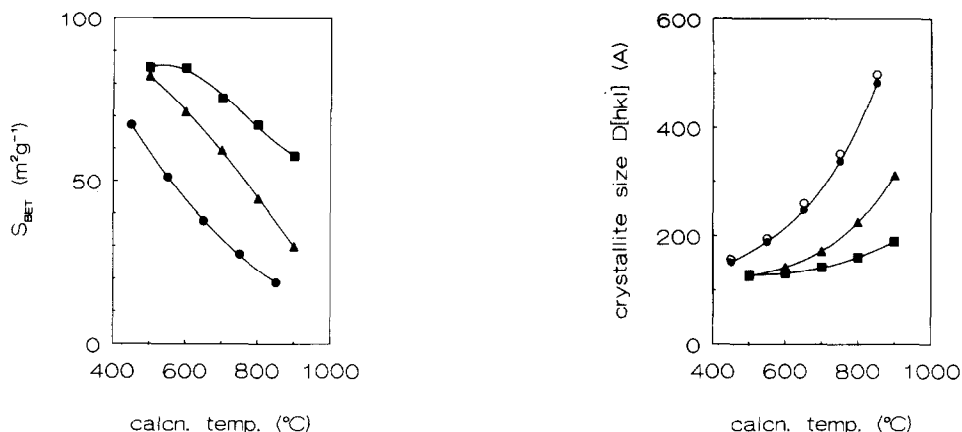


Fig. 7. The variation of the specific BET surface area with calcination temperature for the samples ZrY3 (▲) and ZrLa3 (■); results [8] for a monoclinic sample ZC5-10E (●) are shown for comparison purposes.

Fig. 8. The variation of the crystallite sizes (D_{hkl}) with calcination temperature for the samples ZC5-10E (○ and ●), ZrY3 (▲) and ZrLa3 (■). ●, the size calculated using the (11-1) reflection of the monoclinic phase; ○, the size calculated using the (111) reflection of the monoclinic phase, ▲ and ■, the sizes calculated using the (111) reflection of the tetragonal phase.

Crystallite sizes determined from the micrographs were in close agreement with those obtained by X-ray line-broadening analyses which are given in the last column of Table 2.

The specific surface areas (S_{BET}) of the samples ZrY3 and ZrLa3 calcined at various temperatures are shown in Fig. 7; the results obtained for an undoped single-phase monoclinic zirconia sample, ZC5-10E, prepared by gel precipitation [8], are given for comparison purposes. It is clear that the thermal stability of zirconia is improved considerably by stabilizing its crystal structure in the defect tetragonal form by the incorporation of yttrium or lanthanum cations as solid solutions. The incorporation of lanthanum cations results in a material with particularly high thermal stability, the specific surface area being $58 \text{ m}^2\text{g}^{-1}$ after calcination at 900°C .

Analyses of the X-ray powder diffractograms of the calcined samples showed no discernable reflections other than those pertaining to the tetragonal phase, the inclusion of 5.4 mol-% of Y^{3+} or La^{3+} being sufficient to stabilize the tetragonal phase over the whole range of temperatures studied. The results of X-ray line broadening analyses for each of the samples calcined at various temperatures are shown in Fig. 8, in which the values of the (tetragonal) crystallite sizes are plotted against calcination temperature; the results for the undoped single-phase monoclinic zirconia sample ZC5-10E are included for comparison. It is clear that the process of crystallite growth is significantly inhibited

when yttrium or lanthanum cations are included in solid solution, the incorporation of La^{3+} being much more effective than that of Y^{3+} . These conclusions were confirmed by TEM investigations; Fig. 9 gives representative micrographs at the same magnification for the undoped monoclinic sample ZC5-10E sintered at 850°C (micrograph 9a) and the tetragonal samples ZrY3 and ZrLa3, both sintered at 900°C (micrographs 9b and c respectively). Examination of the micrographs 9b and c together with those of Fig. 6 showed that the bonding between the particles for both the samples ZrY3 and ZrLa3 changed from predominantly point contacts to a predominant sharing of necks as the calcination temperature was increased from 500 or 600°C to 900°C ; these observations are characteristic of the process of Ostwald ripening. As the highest calcination temperature is well below the Tamman temperature of zirconia (ca. 1200°C), the process of crystallite growth and thus of that of inter-crystallite sintering (neck formation and growth) probably occur by a mechanism of surface diffusion. This assumption is in accordance with the work reported by Boutz et al. [22] who investigated the process of grain growth in yttria- and/or ceria-stabilized tetragonal zirconium oxides and concluded that up to a sinter temperature of 900 – 1000°C surface diffusion was the predominant mass transport mechanism. Surface diffusion was also previously established to be the active mass transport mechanism during the sintering of undoped metastable tetragonal or monoclinic zirconia [7,8].

We therefore conclude that the resistance to thermal sintering of zirconia may be increased considerably by the incorporation of 5.4 mol-% of Y^{3+} or La^{3+} in ZrO_2 as solid solutions, the use of lanthanum cations being the most effective. The improvement of the thermal stability appears to be derived from a strong inhibition of the processes of crystallite growth and the accompanying inter-crystallite sintering and thus of the process of mass transport, this most probably occurring by a mechanism of surface diffusion. The flux of mass as a result of surface diffusion is proportional to the product of the (vacancy) diffusion coefficient and the specific surface free energy of the zirconia [42,43]. We believe that the stabilization of the crystal structure of zirconia into the defect tetragonal form by the incorporation of yttrium or lanthanum cations as solid solutions, results in a substantial lowering of both the surface diffusion coefficient and the specific surface free energy of the zirconia. The concept of a lowering of the specific surface free energy of the zirconia is consistent with the results reported by Garvie [44] and by Garvie and Goss [45] who showed that the surface free energy of tetragonal zirconia is intrinsically lower than that of the monoclinic modification. Surface free energy influences are not likely to account for the great difference in effectiveness between Y^{3+} and La^{3+} as textural stabilizers, however.

In undoped zirconium dioxide, the so-called 'Schottky defects' are the most frequently occurring type of defects [21,46] and the Schottky disorder reaction

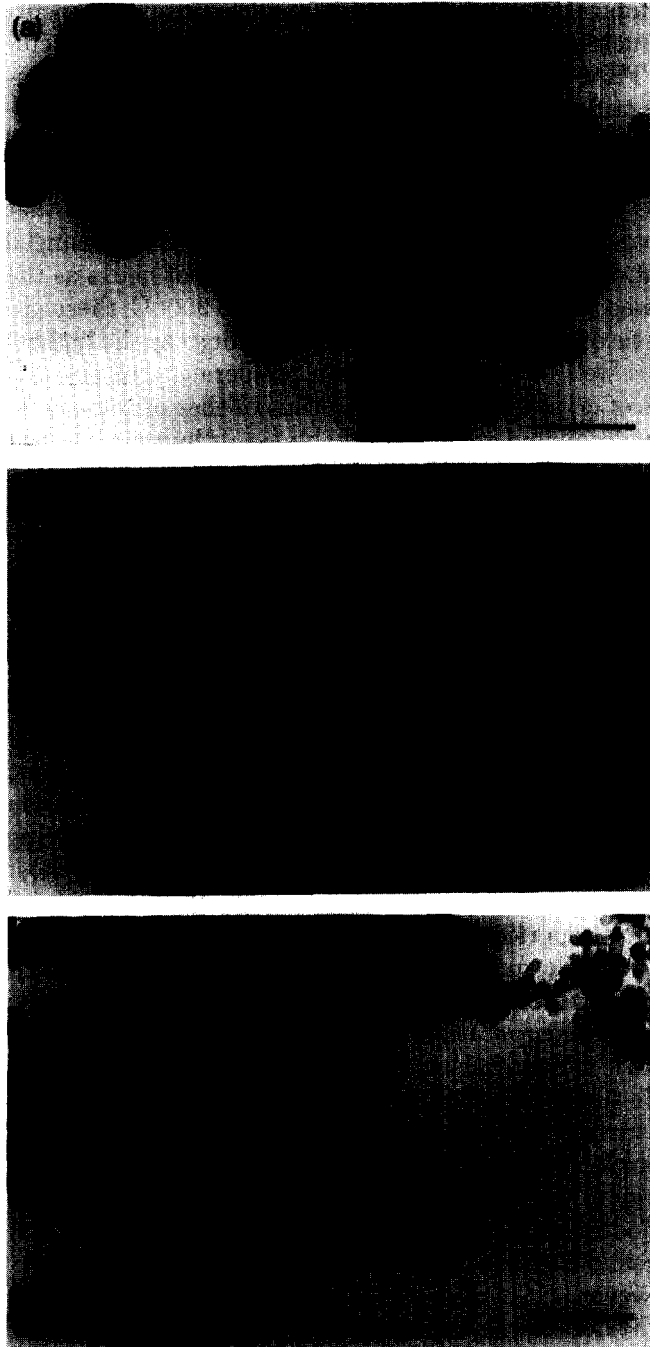


Fig. 9. Transmission electron micrographs of (a) ZC5-10E calcined at 850°C, (b) ZrY3 calcined at 900°C and (c) ZrLa3 calcined at 900°C. The bar indicates a measurement of 100 nm.

(using the Kröger–Vink symbolism) can be represented by eqn. 2:



where $\text{Zr}_{\text{Zr}}^{\times}$ denotes a Zr cation on a Zr lattice site, $\text{O}_{\text{O}}^{\circ}$ denotes an O anion on an O lattice site, $\text{V}_{\text{Zr}}^{\prime\prime\prime}$ denotes a fourfold (negatively) charged zirconium vacancy and $\text{V}_{\text{O}}^{\bullet\bullet}$ denotes a doubly (positively) charged oxygen vacancy. The Schottky equilibrium constant K is given by eqn. 3:

$$K = [\text{V}_{\text{Zr}}^{\prime\prime\prime}][\text{V}_{\text{O}}^{\bullet\bullet}]^2 \quad (3)$$

When zirconia is doped with a trivalent cation M^{3+} (Y^{3+} or La^{3+}), half an oxygen vacancy ($\text{V}_{\text{O}}^{\bullet}$) is produced to preserve electroneutrality. Indeed:

$$4[\text{V}_{\text{Zr}}^{\prime\prime\prime}] + [\text{M}'_{\text{Zr}}] = 2[\text{V}_{\text{O}}^{\bullet}] \quad (4)$$

and as $[\text{V}_{\text{Zr}}^{\prime\prime\prime}]$ is generally much smaller than $[\text{M}'_{\text{Zr}}]$:

$$[\text{M}'_{\text{Zr}}] = 2[\text{V}_{\text{O}}^{\bullet}] \quad (5)$$

According to eqns. 3 and 5, alloying zirconia with Y^{3+} or La^{3+} ions thus results in a decrease in $[\text{V}_{\text{Zr}}^{\prime\prime\prime}]$. Diffusional mass transport in zirconia is determined by the mobility of the cations [13,46,47], the cation diffusion coefficient being about 5 to 6 orders of magnitude smaller than the diffusion coefficient of oxygen, and is thus proportional to the concentration of the cationic vacancies ($[\text{V}_{\text{Zr}}^{\prime\prime\prime}]$). Hence, the incorporation of yttrium or lanthanum cations into the matrix of zirconium dioxide will most certainly result in a lowering of the surface diffusion coefficient; La^{3+} , because of its larger cation size, is likely to lower the surface diffusion coefficient even more than does Y^{3+} [48]. (It is credible, on the basis of the atomistic view of point defects, that differences in the cationic radii will have an influence on the process of mass transfer via surface diffusion, although the effect of cationic radius is not straightforward; may be some associated defects such as $[2\text{M}'_{\text{Zr}}, \text{V}_{\text{O}}^{\bullet}]$ exist, whose stability depends on the cation size.)

It should be noted that the explanation given above is also consistent with that given in connection with our previous results of the influence of additives on the thermal stability of the porous texture of monoclinic zirconia [8]; we showed that the thermal stability of monoclinic zirconia could be improved by the addition, by an impregnation technique, of various oxides among which are Y_2O_3 and La_2O_3 . The best results were obtained with La_2O_3 . The effect of these textural promoters were explained by a model involving mass transport by a mechanism involving surface diffusion. It was suggested that the extent of surface diffusion was strongly influenced by the formation of a (surface) layer of stabilized tetragonal zirconia.

A comparison with γ -alumina and monoclinic zirconia impregnated with lanthanum oxide

Fig. 10 compares the results obtained on ZrLa3 with those presented previously [8] for a high-surface-area commercially available monoclinic zirconia powder (RC100, supplied by Daiichi Kigenso Kagaku Kogyo, Japan); the specific surface areas (S_{BET}) of the undoped sample RC100 and of a RC100 sample which was impregnated with 5.4 mol-% of $\text{LaO}_{1.5}$ together with those of ZrLa3 are plotted against calcination temperature. (An impregnated quantity of 5.4 mol-% $\text{LaO}_{1.5}$ is equivalent to approximately half of the theoretical monolayer capacity given the initial surface area of $71 \text{ m}^2 \text{ g}^{-1}$, half of a monolayer being about the optimum coverage for the stabilization of the textural properties of monoclinic zirconia.) Also included in Fig. 10 are the results obtained with an undoped 'low-surface-area' high purity γ -alumina catalyst support material (type 000-3AQ, supplied by AKZO Chemicals B.V.). Clearly, great progress has been made in the development of high-surface-area zirconium dioxides with well-developed mesoporous textures which are stable under thermal conditions; tetragonal zirconia stabilized by lanthanum cations is particularly promising as a support material for catalysts. However, the stability of the textural properties of stabilized tetragonal zirconium oxide in static air are still not nearly as good as those of high purity γ -alumina.

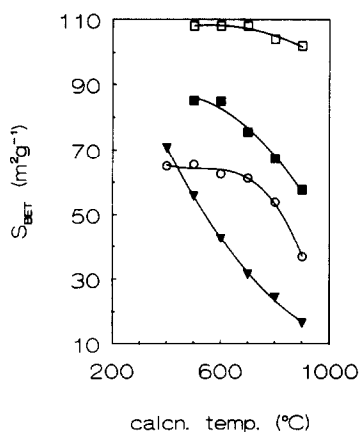


Fig. 10. The variation of the specific BET surface area with calcination temperature for the samples RC100 (∇), RC100 impregnated with 5.4 mol-% $\text{LaO}_{1.5}$ (\circ), ZrLa3 (\blacksquare) and $\gamma\text{-Al}_2\text{O}_3$ (\square).

CONCLUSIONS

1. The incorporation of 5.4 mol-% of Y^{3+} or La^{3+} in ZrO_2 to form solid solutions was found to yield a single-phase of tetragonal zirconium dioxide.

2. The process of crystallization of the initially (X-ray) amorphous hydrous zirconia was shown to be retarded by the incorporation of yttrium or lanthanum cations; the greatest retarding effect was observed with La^{3+} .
3. Upon crystallization, both the samples were found to yield materials which have high specific surface areas with well-developed mesoporous textures which do not contain any microporosity.
4. The thermal stability of the porous texture of zirconia in static air was considerably improved by the stabilization of the crystal structure in the defect tetragonal modification. The incorporation of La^{3+} resulted in a support material which was of particularly remarkable thermal stability.
5. The improvements of the thermal stability were shown to be derived from a strong inhibition of the processes of crystallite growth and the accompanying inter-crystallite sintering and thus of the process of mass transport occurring by a mechanism of surface diffusion.

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