

Effect of Na⁺ Ions on some Properties of Hydrous and Thermally Decomposed Zirconium Oxide

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Sodium-containing zirconium oxide samples (Na ≤ 5.6%), prepared by contacting hydrous zirconium oxide with an Na⁺ solution at a given pH, have been studied by various techniques (XRD, DTA, XPS, surface area determinations and chemical analysis) to elucidate the effect of sodium on surface and bulk properties of zirconium oxide. Both dried (383 K) and thermally treated (≤ 773 K in air) samples have been investigated.

The data show that sodium ions are adsorbed on the hydrous zirconium oxide in different amounts depending on the pH value. For the samples dried at 383 K the adsorbed Na⁺ are atomically dispersed on the hydrous zirconium oxide surface and cause a sintering of the material. For the thermally treated specimens, sodium slows down the crystallization process and affects the crystalline phases. Sodium is present in different locations: (i) atomically dispersed on the surface, (ii) as Na₂O crystals and (iii) incorporated in solid solution. The relative concentration of sodium in these different locations depends on the overall alkaline-ion content. The metastable tetragonal and/or metastable cubic zirconium oxide formation is discussed in terms of different interactions between the sodium species and the oxide matrix.

Keywords: Zirconium oxide; Crystallization; Phase transition; Sintering; Solid solution

Zirconium oxide is a material of considerable scientific and technological importance. It is currently used as a refractory material,¹ a solid electrolyte,² a catalyst,³ or catalyst support,⁴ and with particular additives it is frequently applied in the field of high-technology ceramics.⁵ Hydrous zirconium oxide is an ion exchanger.⁶ Zirconia is usually prepared by the thermal decomposition of a gel obtained by precipitation from solution. When heated at *ca.* 670 K the initially amorphous (to X-rays) material crystallizes, and a mixture of monoclinic (the stable phase below *ca.* 1300 K) and the tetragonal or cubic modification is obtained. The occurrence of the tetragonal metastable form has attracted the interest of many investigators and has been ascribed to different causes such as critical particle size,⁷ lattice strain,⁸ lattice defects⁹ and structural similarity between the amorphous material and the tetragonal modification.¹⁰ Recent reports have shown the influence of chemical factors in the solution from which the gel is precipitated.¹¹ The formation of the metastable cubic phase has received less attention, although it is well documented.^{12,13}

Some years ago a research programme was started in our laboratory to investigate the influence of additives, either retained from the starting materials or intentionally added, on the crystallization process and on the stabilization of the zirconia metastable phases. It was found that the interaction between the foreign species and the zirconium oxide surface led to the slowing down of the crystallization and the stabilization of the tetragonal modification.¹⁴ The purpose of the present study on the interaction of Na⁺ ions is to gain a deeper insight into zirconia crystallization and to gather further information on the impurity effect. We employed a variety of techniques to investigate bulk properties, *i.e.* X-ray diffraction (XRD), differential thermal analysis (DTA) and chemical analysis, as well as surface features, *i.e.* X-ray photoelectron spectroscopy (XPS) and surface-area determinations.

Sodium-doped zirconia systems have been studied previously. Nishizawa *et al.*¹² investigated the effect of NaOH as a mineralizing agent on the zirconia crystallization and transformation under hydrothermal conditions, while Benedetti *et al.*¹³ confirmed the importance of Na⁺ ions in obtaining the cubic phase.

Experimental

Sample Preparation

The hydrous zirconium oxide used as a starting material was prepared by bubbling a stream of ammonia-saturated N₂ from a water solution into a ZrOCl₂ solution (0.35 mol dm⁻³).¹⁴ After separation, the solid was washed (Cl⁻ negative test in the solid) and dried at 383 K for 24 h. A weight loss of 17.1% was obtained by heating at 773 K for 5 h. A second batch of starting hydrous zirconium oxide obtained by a similar procedure was dried at 363 K for 24 h. After heating at 773 K for 5 h, the weight loss amounted to 42.2%.

The sodium-containing samples were prepared by suspending 4 g of hydrous zirconium oxide in a relatively large volume (100 cm³) of aqueous solution at a given pH, which contained a fixed concentration of Na⁺ (1 mol dm⁻³). The pH values (6, 8, 10, 12, 13, 13.5) were obtained using suitable amounts of NaOH, and the final content of Na⁺ was reached by adding the necessary amount of NaCl. The suspension was stirred at room temperature for 72 h to equilibrate the system, and the solid was then filtered from the liquid fraction and dried at 383 K for 24 h.

Samples without sodium were prepared by a similar procedure, the different pH values (7, 9, 12, 13.5) being obtained by adding suitable amounts of ammonia. After filtration, these samples were dried at 383 K for 24 h. Samples with and without sodium are designated as ZNaX(Y) and ZrO₂(Y), respectively, where X = sodium content, wt.%, and Y = pH of the solution. An asterisk identifies the specimens prepared by the hydrous zirconium oxide dried at 363 K.

After filtration, portions of ZNaX(Y) and ZrO₂(Y) were dried at 383 K for various time intervals (≤ 48 h) to study the influence of the drying conditions. For the ZrO₂(13) specimen a fraction was also dried at room temperature *in vacuo* for 8 h.

The samples were studied as-prepared after thermal treatments at a given temperature in air. In particular, the sodium-containing samples were submitted to successive heatings in air at a set temperature and time in order to investigate the effect of sodium on the zirconia crystallization and phase transformation. After each thermal treatment the specimens

were studied by XRD. Overall thermal treatments were as follows: 573 K, 5 h; 593 K, 56 h; 623 K, 18 h; 648 K, 8 h; 673 K, 21 h; 693 K, 113 h; 723 K, 44 h; 748 K, 187 h.

Chemical Analysis

The sodium content was determined by atomic absorption. A known amount of powder was dissolved in 1 cm³ of concentrated (40%) HF solution to obtain the total sodium. The solution was then diluted to bring the sodium concentration in the range 0.2–0.8 ppm. The standard solutions, made from dried (383 K) NaCl, contained ZrO₂ dissolved by HF in a concentration similar to that of the sample. Plastic containers were used for all operations involving HF solutions. The results for the samples ZNaX(Y) dried at 383 K are given in Table 1, those for the specimens heated at 773 K for 5 h in Table 2. For the heated samples, analysis was made not only of the total sodium content, Na_{tot}, but also of the rinsable sodium, Na_{rins}, and that in the solid residue, Na_{sr}. To this end, a known amount of sample (typically 50 mg) was left in contact with 10 cm³ of HCl solution (1 mol dm⁻³) for 5 h and the solid was then separated by filtration and washed. The liquid fractions were collected and used to determine the sodium content. For this determination, the standard solutions contained an HCl concentration similar to that of the samples. After drying, the solid residue was analysed for unrinsed sodium, with a procedure similar to that used for the Na_{tot} determination. To verify the efficiency of the rinsing procedure, a portion of the ZNa3.61(13.5) sample, heated at 773 K, was

submitted to two subsequent rinsing steps. The sodium content was found to be near zero after the second rinsing.

Surface-area Measurements and Porosity

The surface-area determinations were performed by N₂ adsorption at 77 K (B.E.T. method). Pore-size distributions were determined from the corresponding nitrogen adsorption-desorption isotherms at 77 K according to the Brunauer-Mikhail-Bador corrected modelless method¹⁵ applied to the desorption branch.

X-Ray Diffraction

The phase analysis was carried out with a Philips diffractometer (PW 1725) employing Cu-Kα (Ni-filtered) radiation. Two 2θ regions were scanned: 25–35 and 68–78°. In the first region, we observed the high-intensity lines (11̄) and (111) of monoclinic zirconia, in addition to the (101) tetragonal (Teufer cell¹⁶) and/or (111) cubic reflections. These latter two reflections are seen to be superimposed when the corresponding phases are present contemporarily. In the second 2θ range, the (220) tetragonal and the (400) cubic ZrO₂ reflections occur at 74.0 and 74.8° and may be used to discriminate between the two modifications. The 25–35° range was used to determine the onset of the crystallization and to evaluate the fraction of the monoclinic modification, f_m, by the formula

f_m = (I_m(11̄) + I_m(111)) / (I_m(11̄) + I_m(111) + B)

where the I_m(hkl) stands for the intensity of the hkl reflection for the monoclinic phase, B is I_c(111) and/or I_t(101) (c = cubic zirconia, t = tetragonal).

To determine the unit-cell constant for cubic zirconia, a, a Debye-Scherrer camera (i.d. = 114.6 mm) and Cu-Kα (Ni-filtered) radiation were used. The following six reflections in the back-reflection region were measured (θ angle in parentheses): 533 (81.25°); 620 (72.37°); 600 (64.62°); 531 (63.12°); 440 (58.37°); 511 (51.63°) and the graphical method of extrapolation against 1/2[(cos² θ/sin θ) + (cos² θ/θ)] was adopted. The reflections were weak and broad but the occurrence of two reflections at a very large angle leads to accurate determination of the unit-cell constant. An error of ±0.05 cm, as one could expect from observed deviations in three different readings of the same film, produces an error of ±0.0002 nm on a as read from the first diffraction line.

DTA Measurements

DTA measurements were performed on a Perkin-Elmer instrument from room temperature to 1073 K in flowing O₂ (60 cm³ min⁻¹), temperature rate 20 K min⁻¹, using α-Al₂O₃ as a reference. For each experiment the charge (typically 35 mg)

Table 1 SA for zirconium oxide samples with and without sodium, heated at 383 K for different time intervals

samples ^a	drying time/h	SA m ² g ⁻¹
ZrO ₂ (7)	24	360
ZrO ₂ (9)	24	354
ZrO ₂ (12)	24	356
ZrO ₂ (13.5)	24	356
ZrO ₂ (9)*	24	329
ZrO ₂ (13.5)*	24	329
	48	326
ZNa0.74(6)	24	347
ZNa0.92(8)	24	318
ZNa1.09(10)	24	309
ZNa1.91(12)	24	279
ZNa3.61(13.5)	24	232
ZNa3.07(13)	8 ^b	356
ZNa3.07(13)	1	298
	3	306
	48	264
ZNa5.44(13.5)*	24	258
ZNa5.60(13.5)*	24	255
	48	233

^a For designation of samples see text. ^b Vacuum, room temperature.

Table 2 Loss in weight, analytical, surface area and diffraction data for sodium-doped zirconium oxide samples heated in air at 773 K for 5 h

samples ^a	Δ%	Na _{tot} (wt.%)	Na _{rins} (wt.%)	Na _{sr} (wt.%)	Na _{sum} (wt.%)	SA ₇₇₃ m ² g ⁻¹	f _m
ZrO ₂	17.1	—	—	—	—	60	0.82
ZrO ₂ [†]	42.2	—	—	—	—	n.d. ^b	n.d.
ZNa0.74(6)	23.6	0.92	0.92	0.08	1.00	55	0.56
ZNa0.92(8)	23.2	1.15	1.18	0.09	1.27	54	0.51
ZNa1.09(10)	22.8	1.39	1.34	0.15	1.49	47	0.21
ZNa1.91(12)	22.4	2.29	2.08	0.49	2.57	30	0
ZNa3.61(13.5)	21.0	4.42	3.62	0.80	4.42	44	0
ZNa5.60(13.5)*	10.1	6.29	5.42	0.87	6.29	59	0

^a For designation of samples see text. ^b n.d. = not determined.

was covered with 15 mg of α -Al₂O₃. The samples and the reference of comparable volumes were placed in platinum containers.

XPS Measurements

XPS spectra were obtained with a Leybold–Heraeus LHS 10 Spectrometer interfaced with a Hewlett–Packard 2113 B computer, using Al-K α (1486.6 eV) radiation. The finely powdered sample was pressed onto a tantalum plate attached to the sample rod. The spectra were recorded in the sequence Na 1s, O 1s, C 1s, Zr 3d, with Zr 3d_{5/2} at 182.5 eV as reference. Data analysis procedure involved smoothing, and non-linear background subtraction. Peak-area determinations were performed by integration of the appropriate peak after smoothing and background subtraction. The intensity ratio, $I_{\text{Na}}:I_{\text{Zr}}$, was obtained from the corresponding peak areas.

Intensity ratios were also calculated for samples dried at 383 K after treatment at 773 K in air. The Kerkhof and Moulijn model (KM)¹⁷ was applied to predict the $I_{\text{Na}}:I_{\text{Zr}}$ values for the samples dried at 383 K. The porous material is described as stacking sheets of thickness t , where the supported species are assumed to be uniformly distributed. The quantity t is evaluated by the formula $t = [2/(SA_{383} \times d_{\text{HZ}})] \times 10^3$ nm where SA_{383} is the surface area for hydrous zirconium oxide and d_{HZ} the density of hydrous zirconium oxide. The following values were used: $d_{\text{HZ}} = 3.25$ g cm⁻³,¹⁸ total Na content, X , and SA_{383} , from Table 1; for the cross-sections, σ , $\sigma_{\text{Zr}} = 7.044$, $\sigma_{\text{Na}} = 8.506$;¹⁹ for the escape depth in hydrous zirconia, λ , $\lambda_{\text{Zr}} = 2.53$ nm, $\lambda_{\text{Na}} = 1.42$ nm (from Seah²⁰ for ZrO₂·2H₂O and NaOH). We considered three different situations of the Na location for samples heated in air at 773 K:²¹ (i) a non-attenuating overlayer of supported species spread on a semi-infinite support; (ii) the supported species, Na₂O, with a thickness t' , is dispersed over a semi-infinite support causing an exponential attenuation. The thickness t' is evaluated from X-ray line broadening; (iii) part of the Na is present in a homogeneous solid solution. The following values were used, zirconium oxide density at 773 K, $d_{\text{ZrO}_2} = 5.55$ g cm⁻³,²² specific surface area, SA_{773} , and total Na content, Na_{tot} , as reported in Table 2; cross-sections as above; escape depth, $\lambda_{\text{Zr}} = 2.2$ nm, $\lambda_{\text{Na}} = 1.23$ nm (from ref. 20 for ZrO₂ and Na₂O).

Results

Chemical Analysis

Table 1 shows that for ZNaX(Y) samples the total sodium content, X , increases with the pH of preparation, Y . Moreover, two samples prepared at pH 13.5 show that the sodium uptake is higher for the material dried at 363 K. For samples prepared by using hydrous zirconium oxide dried at 383 K, the following values for the total sodium content (wt.%) are obtained (pH in parentheses): 0.74 (6), 0.92 (8), 1.09 (10), 1.91 (12), 3.03 (13), 3.61 (13.5); for the two specimens prepared from hydrous zirconium oxide dried at 363 K the sodium content is 5.64 (13.5) and 5.68 (13.5). As noted by Inoue and Yamazaki,²³ the ion-exchange capacity for hydrous zirconium oxide depends on the thermal treatment to which the solid is submitted prior to the ion-exchange, and this capacity decreases as the temperature increases.

Table 2 shows the data for samples treated at 773 K, column 3 giving the total sodium content. For each specimen the value agrees with that deduced from the as-prepared samples, taking into account the weight loss from heating at 773 K, column 2. Columns 4 and 5 show the amount of sodium that may be rinsed away, and that left in the solid residue,

respectively, and their sum is given in column 6. For each sample the value of column 6 agrees, within experimental error, with the total sodium reported in column 3. A portion of the ZNa(13.5) sample treated at 773 K was ground and then rinsed in order to study the effect of the grinding on the rinsable sodium. Sodium content in the ground solid was observed to be almost zero.

Surface Area and Porosity

The hydrous zirconium oxide used for the sample preparation has a quite high specific surface area and appears microporous. In fact, according to Livage *et al.*¹⁰ this material is formed by platelets *ca.* 2–6 nm in diameter and a few monolayers in thickness. In the xerogel state these thin platelets are packed in a disordered manner with numerous voids, which give rise to a porous structure. As a consequence, the surface area values obtained by the B.E.T. method are an over-estimation. A more realistic value for the surface area may be obtained by the t -plot method (S_t).²⁴ For the starting zirconium oxide the following values are obtained: $S_{\text{BET}} = 360$ m² g⁻¹, $S_t = 330$ m² g⁻¹; therefore the over-estimation due to the microporosity on the S_{BET} amounts to *ca.* 10%. The pore distribution is characterized by a consistent fraction of pores with an average radius <2.0 nm.⁴ These textural properties remain unchanged for the sodium-free samples dried at 383 K; in particular the specific surface area does not change with pH or with the drying time, see Table 1. A change in the surface area and in the pore distribution is observed for the sodium-containing specimens. With increasing pH the surface area decreases (Table 1) and the pore distribution shifts to higher radius values as shown in Fig. 1. The specific surface area decreases with the drying time (see Table 1).

DT Analysis

DTA experiments for the dehydration and for the crystallization of the different hydrous zirconium oxide samples show an endothermic peak in the temperature range 363–423 K due to dehydration and an exothermic effect at *ca.* 700 K. The latter peak is typical of hydrous zirconium oxide and is due to the crystallization process.²⁵ It remains unchanged for all the ZrO₂(Y) samples. By contrast, the ZNaX(Y) specimens prepared at increasing pH show a progressive shift of the crystallization peak to higher temperatures and a broadening as the value of X increases (see Fig. 2).

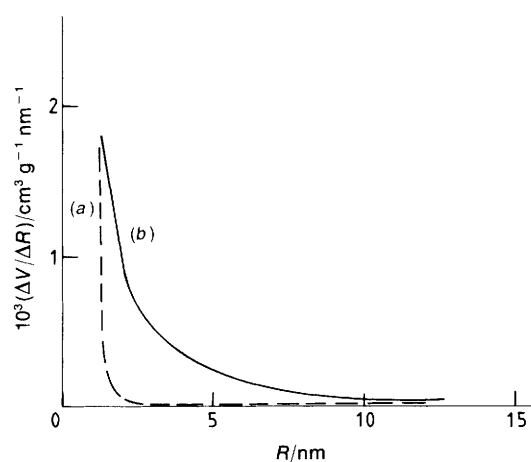


Fig. 1 The shift of pore-size distribution with addition of sodium: (a) ZrO₂(383) from ref. 4; (b) ZNa_{3.61}(13.5) dried at 383 K for 24 h

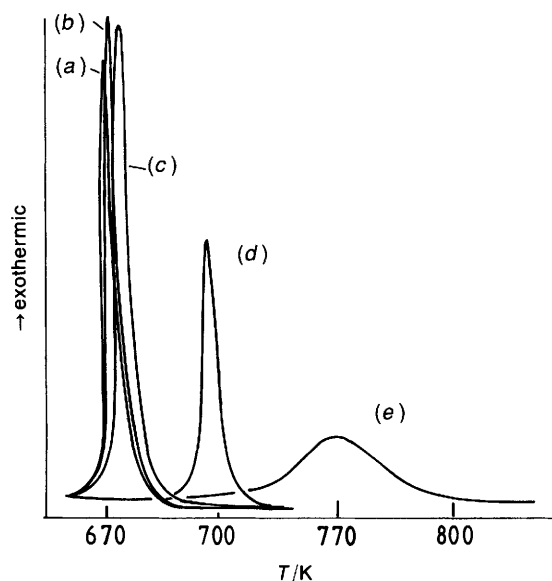


Fig. 2 DTA exothermic peak due to the crystallization of ZrO_2 (a) hydrous zirconium oxide; (b) $\text{ZNa}_{0.74}(6)$; (c) $\text{ZNa}_{1.09}(10)$; (d) $\text{ZNa}_{1.91}(12)$; (e) $\text{ZNa}_{3.61}(13.5)$

X-Ray Measurements

The sodium-containing samples, heated at 573 K for 5 h, are amorphous to X-ray diffraction. At higher temperatures crystalline phases appear and the crystallization depends on both the temperature and the heating time. At constant temperature, the heating time required for the crystallization increases with Na content. Thus for the following samples the specified times required at 598 K for the appearance of the crystalline phases are: $\text{ZNa}_{0.74}(6)$ and $\text{ZNa}_{0.92}(8)$, 12 h; $\text{ZNa}_{1.09}(10)$, 20 h; $\text{ZNa}_{1.91}(12)$, 34 h. At constant heating time and temperature the extent of crystallization and the crystalline phase formed depend on the sodium content. This is illustrated by Fig. 3 showing the diffraction patterns for samples heated 648 K for 8 h, after a previous treatment in steps at 573 K for 5 h, 598 K for 56 h, and 623 K for 18 h. For the $\text{ZNa}_{3.61}(13.5)$ sample the most intense reflection only is detectable. A comparison of the diffraction lines in the 2θ

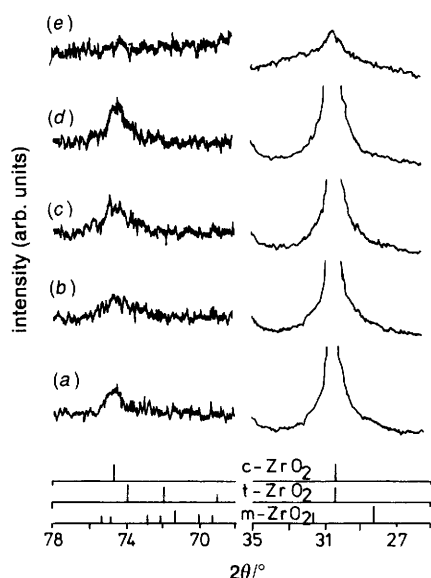


Fig. 3 Extent of crystallization and crystalline phases for zirconium oxide samples with different sodium content. (a) $\text{ZNa}_{0.74}(6)$; (b) $\text{ZNa}_{0.92}(8)$; (c) $\text{ZNa}_{1.09}(10)$; (d) $\text{ZNa}_{1.91}(12)$; (e) $\text{ZNa}_{3.61}(13.5)$. All samples were heated at 648 K for 8 h, after successive steps at 573 K, 5 h; 598 K, 56 h; 623 K, 18 h

ranges 25–35 and 68–76° with those of the different zirconia polymorphs shows that the formed crystalline phase is mostly cubic zirconia. The relative concentration of the different phases is clearly visible at higher temperatures, where the monoclinic modification also appears. The transformation temperature depends on the sodium content: more dilute samples transform at lower temperature, as shown in Fig. 4 where the X-ray patterns of samples submitted to the overall treatment (573 K, 5 h; 598 K, 56 h; 623 K, 18 h; 648 K, 8 h; 673 K, 21 h; 693 K, 113 h; 723 K, 44 h; 748 K, 187 h) are reported. Monoclinic zirconia is clearly present in specimens with a sodium content of up to 1.09, while it is absent in samples of higher concentrations. For $\text{ZNa}_{1.91}(12)$ the reflection at $2\theta = 74.25^\circ$ is asymmetric, which indicates the presence of tetragonal or a mixture of tetragonal and cubic zirconia; on the other hand for $\text{ZNa}_{3.61}(13.5)$ and for the more concentrated sample (not shown in Fig. 4) only cubic zirconia lines were detected.

The cubic unit-cell parameter a of both $\text{ZNa}_{3.61}(13.5)$ and $\text{ZNa}_{5.60}(13.5)^*$, heated at 773 for 5 h in air, was found to be 0.5114 ± 0.0002 nm. This value can be compared with that given by Katz²⁶ for cubic zirconia, prepared at $T < 1273$ K, i.e. $a = 0.510$ nm.²⁶ However, as already noted,¹³ the latter value may refer to zirconia containing sodium impurities, since NaOH was involved in the preparation of the precursor. An alternative method of obtaining information on the lattice constant for undoped cubic ZrO_2 is by extrapolation to zero from the plot of the lattice constants of solid solutions *vs.* dopant concentration. This method was used for the systems $\text{Fe}_2\text{O}_3\text{--ZrO}_2$ and $\text{La}_2\text{O}_3\text{--ZrO}_2$ and gave the values^{27,28} 0.5085 and 0.5080 nm, respectively. Both these values are lower than those measured for the more concentrated $\text{ZNa}_X(13.5)$ samples heated at 773 K for 5 h, and are also lower than the value reported previously by Katz. The average value of the extrapolated data is taken as the unit-cell constant for pure cubic zirconia.

From Table 3 it is evident that the sample $\text{ZNa}_{3.61}(13.5)$ heated at 773 K for 5 h, also contains Na_2O . Sodium oxide is also present in the diffraction pattern of $\text{ZNa}_{5.60}(13.5)^*$

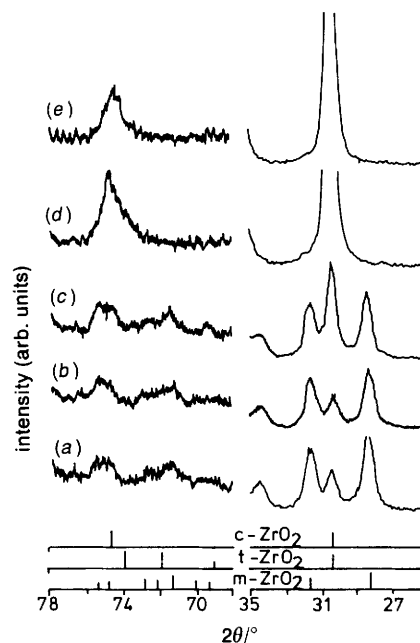


Fig. 4 Crystalline phases for zirconium oxide samples with different sodium content. (a) $\text{ZNa}_{0.74}(6)$; (b) $\text{ZNa}_{0.92}(8)$; (c) $\text{ZNa}_{1.09}(10)$; (d) $\text{ZNa}_{1.91}(12)$; (e) $\text{ZNa}_{3.61}(13.5)$. All samples were heated at 743 K for 187 h, after successive steps at 573 K, 5 h; 598 K, 56 h; 623 K, 18 h; 648 K, 8 h; 673 K, 21 h; 698 K, 113 h; 723 K, 44 h

Table 3 XRD pattern for the ZNa3.61(13.5) sample, heated at 773 for 5 h

<i>d</i> _{exp} /nm	<i>I</i>	cubic ZrO ₂ ^a			Na ₂ O ^b	
		<i>d</i> /nm	<i>I</i> / <i>I</i> ₀	<i>h k l</i>	<i>d</i> /nm	<i>I</i> / <i>I</i> ₀
0.323	vw				0.321	33
0.293	vs	0.293	100	1 1 1		
0.280	vw				0.278	41
0.254	m	0.255	25	2 0 0		
0.198	vw				0.196	100
0.180	s	0.1801	50	2 2 0		
					0.1677	5
					0.1605	7
0.1537	ms	0.1534	20	3 1 1		
0.1472	w	0.1471	5	2 2 2		
					0.1390	10
0.1275	w	0.1270	5	4 0 0	0.1275	1
					0.1243	5
0.1170	w	0.1167	5	3 3 1		
0.1140	w	0.1350	5	4 2 0	0.1135	9
0.1040	w	0.1038	1	4 2 2		
0.0983	w	0.09796	1	5 1 1	0.0983	2
0.0903	w	0.08998	1	4 4 0		
0.0863	w	0.08604	1	5 3 1		
0.0852	vw	0.08533	(c)	6 0 0		
0.0806	w	0.08048	1	6 2 0		

^a ASTM Card 27-997; ^b ASTM Card 23-528; ^c not reported in the ASTM Card and calculated on the basis of *a*=0.5114 nm.

submitted to a similar thermal treatment. By measuring the peak area of the (220) reflections both for cubic ZrO₂ and for Na₂O, as a first approximation the percentage of Na₂O was estimated to be *ca.* 1 and 2% for ZNa3.61(13.5) and ZNa5.60(13.5)*, respectively. The evaluation was performed by the formula

$$\% \text{ Na}_2\text{O} = [A(\text{Na}_2\text{O})_{220}/100]/[A(\text{ZrO}_2)_{220}/50]$$

where *A*(Na₂O)₂₂₀ and *A*(ZrO₂)₂₂₀ are the diffraction peak areas for the Na₂O and ZrO₂ and 100 and 50 their reported intensities. The detectability of Na₂O by X-ray diffraction gives a lower limit of 5 nm for the Na₂O crystallite size, but the diffraction line broadening gave an average size of less than 20 nm. A value of 10 nm was therefore used to calculate the XPS intensity ratio (see below). No sodium oxide lines were visible in either sample after rinsing with water.

XPS Measurements

Fig. 5 shows the experimental XPS intensity ratios for the ZNaX(Y) samples dried at 383 K as a function of the Na surface concentration (Na atoms nm⁻²), calculated from the analytical data and from the surface-area values (Table 1). A linear correlation is found up to 4.08 Na atoms nm⁻², ZNa3.61(13.5), but thereafter a saturation effect appears. Also shown in Fig. 5 are the calculated intensity ratios, based on the KM model. In the concentration range up to 4.08 Na atoms nm⁻² the calculated values agree well with the experimental ones, which indicates a good dispersion of sodium. It should be noted that the calculated intensity ratio values do not change appreciably if the surface area values are decreased by 10%, which takes into account the over-estimation due to microporosity.

Fig. 6 shows the *I*_{Na}:*I*_{Zr} values for samples heated at 773 K for 5 h in air *vs.* the total sodium content. The abscissa, Na atoms nm⁻², was calculated from the appropriate sodium content and specific surface area, Table 2, columns 3 and 7, respectively. In the same figure *I*_{Na}:*I*_{Zr} values, calculated by the non-attenuating overlayer spread on the semi-infinite support model are also reported. The comparison between

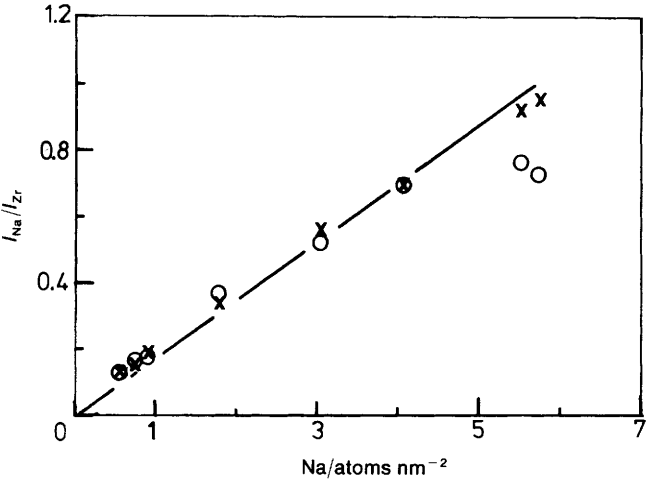


Fig. 5 XPS intensity ratio *I*_{Na}:*I*_{Zr} *vs.* sodium surface concentration (Na atoms nm⁻²) for ZNaX(Y) samples dried at 383 K. (○) Experimental; (×) calculated values

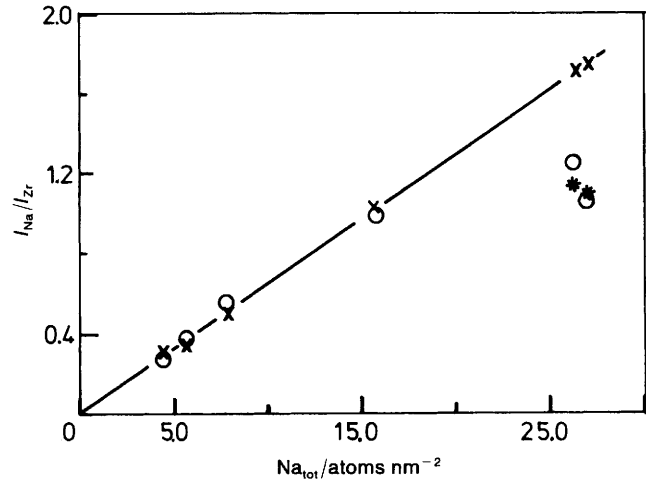


Fig. 6 XPS intensity ratio *I*_{Na}:*I*_{Zr} *vs.* sodium surface concentration (Na atoms nm⁻²) for ZNaX(Y) samples heated at 773 K for 5 h, in air. (○) Experimental; (×) calculated by considering sodium spread as a non-attenuating overlayer on a semi-infinite support; (*) calculated by summing the contribution from atomically dispersed sodium, from Na₂O microcrystals (10 nm) and from Na⁺ incorporated in solid solution

experimental and calculated values shows good agreement for all specimens with the exception of the most concentrated ones.

Discussion

The morphological properties of hydrous zirconium oxide and the ensuing crystallization and phase-transformation process depend upon the nature of the solution left in contact.

As-prepared Samples

As noted, hydrous zirconium oxide precipitates of high surface area are powerful adsorbents and ion-exchangers.^{6,23,29} In particular, sodium ions are adsorbed, the amount depending on the pH of the solution. The pH dependence, studied by Inoue and Yamazaki,²³ is accounted for by the fact that the pH of the solution in contact with a solid of a given isoelectric point, *IP*, controls the polarization of the solid surface, and thus its adsorption ability.²⁹ The higher the pH with regard to the *IP* value, the more negative the oxide surface and the larger the amount of cation adsorption.

During the drying process at 383 K, the adsorbed sodium ions remain automatically dispersed on the support surface, and react with nearby hydroxyl groups. A high dispersion of sodium on the hydrous zirconium oxide surface is supported by the XPS measurements, see Fig. 5.

The presence of sodium on the hydrous zirconium oxide surface affects the morphological properties of this material, as shown by the decrease in surface area for the ZNaX(Y) samples submitted to similar drying processes (24 h at 383 K), Table 1. This surface-area decrease with increasing sodium content may be ascribed to the presence of the alkaline ions, and not merely to the basic ambience of the solution in contact with the solid during preparation. In fact, no surface area decrease is observed for the samples ZrO₂(Y), which are prepared by contact between the hydrous zirconium oxide and a sodium-free solution at a given pH, followed by drying at 383 K for 24 h, see Table 1. It must be also noted that the surface-area decrease is a process which takes place during the drying stage at 383 K, as demonstrated by the data collected for the different fractions of the ZNa3.07(13) sample. In fact, while no surface-area contraction is observed for the sample dried *in vacuo* at room temperature for 8 h, a time-dependent shrinkage was measured for the fractions dried at 383 K. The influence of time at 383 K is confirmed by the fractions of the ZNa5.60(13.5)* sample dried 24 and 48 h, respectively.

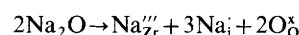
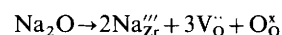
The influence of sodium on the sintering of hydrous zirconium oxide may be accounted for by the fact that the alkaline ions can affect the formation of hydrogen bonds between particles in close contact. As recently discussed by Kaliszewski and Heuer,³⁰ excess water present in the hydrous oxide forms hydrogen bonds with the hydroxyl groups of the gel. Bridging by hydrogen bonding of water to two terminal hydroxyl groups occurs for particles in close contact. During the drying process these bridging water molecules are lost, and hydrogen bonds form between the terminal hydroxyl groups of different particles. If the drying process is continued, further water is lost, and formation of chemical bonds between different particles takes place. The above hypothesis serves to explain the influence of sodium on sintering. Sodium ions adsorbed on the hydrous zirconium oxide surface can enhance the hydrogen-bond formation since their electronegativity is lower than that of hydrogen. They can therefore induce a higher negative charge on the oxygen involved in the hydrogen bonding. As a result, the sintering between different hydrous zirconium particles is favoured. If we consider the simple model of spherical particles, we see that the initial sintering results in the growth of the neck region between the particles. As a consequence, the smaller interparticle voids disappear and the fraction of wider pores increases, in agreement with the pore distribution for dried samples, Fig. 1.

Thermally Treated Samples

When the ZNaX(Y) samples are heated at increasing temperature, several phenomena occur. Further water is lost, sodium hydroxide is transformed into sodium oxide, the amorphous material crystallizes and a fraction of sodium is incorporated in solid solution. An indication of the formation of the solid solution comes from the results of the chemical analysis, see Table 2. For samples heated at 773 K, only a fraction of sodium remains on the surface and this can be rinsed away (column 4). Note that the sodium remaining in the solid residue (column 5) cannot be accounted for by inefficient rinsing or by the presence of sodium on surface regions (interstices among particles) not reached by the washing liquid, since a near-zero sodium content was obtained after a second washing treatment, and only a very small increase in the

rinsable sodium was found for the more concentrated sample submitted to a grinding process before washing. On the other hand, the formation of the solid solution is demonstrated by the higher value of the unit-cell constant of cubic zirconia for the samples ZNa3.61(13.5) and ZNa5.60(13.5)* heated at 773 K, compared with that reported for undoped zirconia. The *a* values of these samples are nearly identical as expected if we assume that their similar Na_{sr} content (Table 2, column 5) corresponds to sodium in solid solution.

For Ca-containing zirconium oxide solid solutions prepared at high temperatures the only defects experimentally confirmed involve interstitial cations and anionic vacancies.³¹ If the present case is analogous, the sodium incorporation may be described by the reactions (Kröger notation³²).



where Na_{Zr}'' is a negatively charged substitutional defect, Na_i[•] a positively charged interstitial imperfection, V_O[•] a positively charged oxygen vacancy and O_O[×] an oxygen atom on a normal anionic lattice site. Thus the solid solution is represented by the formula

$$[\text{Na}_{(x-y)}\text{Zr}_{(1-x)}]_s[\text{Na}_y]_i[\text{O}_{2-(3/2)(x-y)+y/2}\square_{(3/2)(x-y)-y/2}] \quad (1)$$

where *s* and *i* stand for substitutional and interstitial cations, □ for anionic vacancies, while *x* and *y* represent the mole fractions of total and interstitial sodium, respectively. For such a solid solution the unit-cell constant may be calculated by the relation derived for a fluorite-type structure³³

$$a = 4/[(1-y)^{3/2}]\{xr(\text{Na}^+) + (1-x)r(\text{Zr}^{4+}) + (1-y)r(\text{O}^{2-})_{\text{eff}}\} \quad (2)$$

where 1 − *y* is a normalization factor derived from the fact that 1 − *y* ZrO₂ formula units are considered, *r*(O^{2−})_{eff} is the effective O^{2−} ionic radius given by *r*(O^{2−})_{eff} = *r*(O^{2−})(1 − number of anionic vacancies/anion sites)^{1/3}, *r*(O^{2−}), *r*(Na⁺) and *r*(Zr⁴⁺) are the O^{2−}, Na⁺ and Zr⁴⁺ ionic radii, respectively. By recalling (1), the relation (2) becomes

$$a = 4/[(1-y)^{3/2}]\{xr(\text{Na}^+) + (1-x)r(\text{Zr}^{4+}) + (1-y)r(\text{O}^{2-})[1 - (3x - 4y)/4(1-y)]^{1/3}\}$$

Note that for the vacancy model, *y* = 0, while for the interstitial one, *y* = 3*x*/4. If we recall that for the sample ZNa3.61(13.5), heated at 773 K, the sodium content in solid solution is 0.80 wt.%, corresponding to *x* = 0.042, and if we take the following values³⁴ for the ionic radii *r*_{Na⁺} = 0.118 nm, *r*_{Zr⁴⁺} = 0.084 nm (VIII co-ordination), *r*_{O^{2−}} = 0.1374 nm, the calculation gives *a* = 0.5112 nm for the vacancy model and *a* = 0.5210 nm for the interstitial one. The experimental value *a* = 0.5114 ± 0.0002 nm points to the vacancy model as the most appropriate.

The incorporation of sodium in cubic ZrO₂ and the ensuing lattice expansion is supported by literature data. A unit-cell constant *a* = 0.5116 ± 0.0002 nm was measured for a sample heated at 708 K for 24 h, which contained 3% of sodium as total content.¹³ In that case the total sodium present was assumed to be in solid solution (no test for rinsable sodium was performed). However, as shown in the present investigation, probably only a fraction is incorporated, so that the agreement with our data may be considered good. The formation of the solid solution by incorporation of a fraction of sodium is consistent with the results of the XPS measurements. The disagreement between the experimental and calculated XPS intensity ratio for the most concentrated samples, shown in Fig. 6, indicates that in these samples not all the sodium atoms are equally detectable by XPS. The model used

for the calculation considers the sodium species to be totally dispersed on the support surface, while, as discussed above, a fraction of sodium is incorporated in solid solution. In addition, the XRD patterns reveal that a small amount of Na_2O is also present. Both the sodium incorporated into the lattice and that present as segregated Na_2O are expected to give a decreased contribution to the intensity ratio if compared with a surface-dispersed situation. Accordingly, the intensity ratio can be obtained by summing the contributions (i) from sodium atomically dispersed on the surface; (ii) from sodium present as Na_2O microcrystals (10 nm in size) and (iii) from that incorporated in solid solution. For the $\text{ZNa}3.61(13.5)$, $\text{Na}_{\text{tot}} = 4.42\%$ (Table 2, column 3), the sodium content on the surface is 3.62% (Table 2, column 4). By subtracting the amount present as Na_2O , taken as 1.0% for the sake of the calculation, the fraction of sodium atomically dispersed becomes 2.62%. Then the calculated intensity ratio is $1.00 + 0.04 + 0.09 = 1.13$. The same procedure for the $\text{ZNa}5.60(13.5)^*$ sample gives the following values: $0.97 + 0.05 + 0.10 = 1.12$. Both estimated values show good agreement with the experimental ones, 1.15 and 1.05, respectively (Fig. 6).

The presence of sodium affects the solid-state processes taking place during heat treatment. When undoped hydrous zirconium oxide is heated a very rapid crystallization takes place at *ca.* 720 K (Fig. 2) giving a mixture of tetragonal and monoclinic phases. After heating at 773 K for 5 h, a monoclinic fraction, $f_m = 0.81$ is found, see Table 2. For Na-doped zirconium oxide, DTA data show that as the sodium content increases, crystallization occurs at higher temperatures (Fig. 2). The fraction of the monoclinic modification in the crystallized material decreases (Table 2) and, in the more concentrated samples, cubic zirconia is formed preferentially. In addition, the cubic–monoclinic phase transformation occurs at higher temperature.

The stabilization of the cubic modification, when a significant Na^+ amount is incorporated in ZrO_2 is supported in the literature. Nishizawa *et al.*,¹² studied hydrothermally prepared sodium-doped samples. These authors did not explicitly report the sodium content, but the value of the unit-cell parameter reported ($a = 0.5119$ nm) suggests that the sodium concentration in solid solution in their sample may be close to that found in the present study. As already noted, cubic zirconia with $a = 0.5116$ nm, was also found by Benedetti and co-workers^{13,35} for a sample heated at 773 K. A more complex situation is encountered if the content of the incorporated sodium is not sufficient to fully stabilize the cubic phase, since tetragonal or a mixture of tetragonal and cubic is formed. This occurs for the sample $\text{ZNa}1.91(12)$ heated at 773 K (sodium in solid solution ≤ 0.49 , Table 2), and is confirmed by Benedetti *et al.*³⁵ who reported the tetragonal phase only for a sample containing 0.5% as total sodium. Indeed, the two phases when contemporaneously present, are not easily distinguishable.

The stabilization of otherwise unstable zirconia phases (tetragonal and cubic) at low temperature by addition of foreign species has been studied at length. The numerous data reported in the literature show that when a foreign species is incorporated in solid solution, at increasing concentration, first the tetragonal and then the cubic phase are formed. If the added species interacts with the surface the tetragonal modification is obtained. In addition to Na^+ , solid solutions and formation of tetragonal or cubic ZrO_2 have been reported for Ca^{2+} , Ni^{2+} , Fe^{3+} , Rh^{3+} and La^{3+} (see ref. 36, 37, 27, 28 respectively) while the tetragonal modification has been reported for systems where Mo^{VI} , Cr^{VI} , Cl^- , ReO_4^- , W^{VI} , SO_4^{2-} were supported on the zirconium oxide surface (see ref. 38, 4, 12, 39, 40–43). In this context we should recall that

X-ray amorphous zirconium oxide is formed by minute crystallites whose structure has been reported to be tetragonal¹⁰ or cubic.⁴⁴ The tetragonal modification was detected by neutron diffraction on samples previously heated at 623 K while the cubic one was revealed by electron diffraction on ultra-high-purity submicrometre zirconium oxide prepared by thermal decomposition of alkoxides (temperature range 598–723 K). The latter material was heated up to 573 K for 150 h and proved to be in transition from the X-ray amorphous to the crystalline state, in the form of cubic modification.⁴⁵ After subsequent heating at 578 K for 150 h the tetragonal modification appeared, but treatments at higher temperature yielded the monoclinic form. We should stress that the metastable cubic–metastable tetragonal transition takes place in a narrow temperature range (573–578 K in the case reported) and this explains why the cubic phase is not often observed.

It is now possible to advance an explanation for the different effect of additives on the crystallization behaviour of amorphous zirconium oxide. It is known that the presence of additives lowers the crystallization rate and, if the added species is incorporated in solid solution when the cubic structure is present, this phase remains stabilized in a wider temperature range. The detection of the cubic phase only requires a certain content of the guest ions in solid solution. For lower concentrations the tetragonal modification will also appear. On the other hand, if the interaction of the added species is limited to the surface, the slowing down of the crystallization is still observed; however, since no solid solution is formed, the cubic form is not stabilized and the tetragonal modification appears and persists in a wide temperature range.

Conclusions

The data show that Na^+ ions adsorbed on hydrous zirconium oxide have a marked effect on sintering, crystallization and phase transformation. When other factors are constant, the ionic adsorption process is controlled by the pH of the solution in contact with the solid. Since the hydrous zirconium oxide is often prepared by precipitation from a solution at a given pH, usually fixed by a particular acid or base, great caution is needed in correlating such effects to the solution pH,^{11,46} since the correlation may be only indirect.

The dispersed Na^+ ions also play an important role in the solid-state processes taking place during the subsequent heat treatment. In fact, the added ions are partly incorporated into the zirconia structure, which slows down the crystallization process and stabilizes the cubic modification. Similar to other solid solutions based on zirconia, if the amount of the incorporated ion is insufficient, tetragonal zirconia or a mixture of cubic and tetragonal zirconia, appears.

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