

## Review

# Chemistry of zirconia and its use in chromatography

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### ABSTRACT

The purpose of this review is to shed some light on the complex properties of zirconia's surface chemistry in order to better understand its behaviour under chromatographic conditions. We emphasize the great differences between the much better known chemistry of a silica surface and the chemistry of zirconia's surface. The review describes both the physical and chemical properties of zirconium dioxide from a chromatographic point of view. The chemistry of monoclinic zirconia surface is developed from its underlying crystalline structure. The paper describes the dependence of the specific surface area, pore volume, porosity and mechanical strength on thermal treatment. Methods of synthesis of chromatographically useful zirconia are outlined. The review also covers the adsorption properties of zirconia at both gas–solid and liquid–solid interfaces. Adsorption of water, carbon dioxide, carbon monoxide and ammonia are described and the controversies concerning the surface concentration of adsorption sites are presented. The complex chemistry of a zirconia surface is pointed out and the importance of ligand exchange reactions is emphasized. In contrast to a silica surface, ligand exchange plays an important role in liquid chromatographic applications of zirconia. Strong, hard Lewis acid sites, present on a zirconia surface, can interact with hard Lewis bases and these interactions, sometimes troublesome, can be successfully exploited even for protein separations. Zirconia's surface can be modified in many ways: dynamically, by addition of competing Lewis bases to the mobile phase, or permanently, by covering its surface with polymers or by depositing carbon.

The review also shows that the main difficulty in achieving a wider variety of applications is probably our lack of knowledge and poor understanding of zirconia's surface chemistry.

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## CONTENTS

1. Introduction .....	230
2. Physical properties .....	232
2.1. Precipitation of zirconia —dependence of physical properties on conditions .....	232
2.2. Crystallinity .....	233
2.2.1. Monoclinic zirconia and the origin of surface activity .....	234
2.3. Surface area .....	236
2.4. Density of zirconia .....	238
2.5. Pore volume and porosity .....	238
2.6. Pore size distribution and shape of the pores .....	239
2.7. Mechanical strength .....	240
2.8. Purity of zirconia .....	241
2.9. Commercially available zirconia powders .....	242
2.10. Requirements for and achievements in HPLC-grade zirconia technology .....	242
3. Chemical properties .....	245
3.1. Chemical stability .....	245
3.2. Adsorption properties —gas–solid interface .....	246
3.2.1. Water and hydroxyls .....	247
3.2.1.1. Interactions of hydroxyl groups with alcohols .....	248
3.2.1.2. Acidity of the surface hydroxyls .....	249
3.2.1.3. Elimination of coordinatively bonded water .....	250
3.2.2. Carbon dioxide adsorption on the zirconia surface .....	251
3.2.3. Carbon monoxide adsorption .....	253
3.2.4. Bases: ammonia and pyridine .....	254
3.3. Surface concentration of acid and base adsorption sites in gas–solid systems .....	255
3.4. Zirconia as a stationary phase in gas chromatography .....	257
3.5. Adsorption: liquid–solid interface .....	257
3.5.1. Introduction .....	257
3.5.2. Point of zero charge .....	258
3.5.3. Surface equilibria .....	260
3.5.4. Borate adsorption .....	263
3.5.5. Complexes with fluoride .....	263
3.5.6. Complexes with phosphates .....	263
3.6. Zirconia in liquid chromatography .....	265
3.6.1. Eluotropic series .....	265
3.6.2. Chemical, dynamic modification .....	267
3.6.3. Chemical, permanent modification .....	272
3.6.4. Physically screened zirconia particles .....	274
3.6.4.1. Polybutadiene-coated zirconia .....	274
3.6.4.2. Polystyrene-coated zirconia .....	275
3.6.4.3. Carbon-coated zirconia .....	275
3.6.4.4. Polymer-coated carbon-clad zirconia .....	276
3.6.5. Other zirconia applications in chromatography .....	277
4. Conclusions .....	277
5. Acknowledgements .....	278
References .....	278

## 1. INTRODUCTION

Zirconia, *i.e.* zirconium dioxide, exists in many crystallographic and amorphous forms. This material has interesting properties and it has numerous applications in modern technology [1,2]. We would like to draw attention to a new, promising application of zirconia: as a column

packing material for high-performance liquid chromatography (HPLC). The ideal HPLC support particle should be energetically homogeneous, have a high surface area on which a wide variety of chemical moieties can be irreversibly and inalterably deposited to provide useful selectivity for a number of separation problems. It should be physically and chemically stable over a

wide range in pressure, pH, temperature and solvent conditions. It should be available in a variety of particle diameters as well as pore sizes and volumes.

It is clear from the literature describing the deficiencies of existing supports and the extensive current interest in the development, evaluation and optimization of “new and improved” supports for HPLC that presently available supports remain far from this ideal.

Properties of the ideal chromatographic support are listed in Table 1. Although silica and modified silicas are the most widely used and most useful HPLC supports, it is well known that silica and bonded phase silicas are not stable outside the range of pH 2 to approximately 8 [3–8]. Above pH 8 silica is subject to attack by alkali and it dissolves. Below approximately pH 2, the siloxane linkages which hold bonded phases to silica are subject to hydrolytic attack and are slowly removed from the surface [9–11]. The dissolution of silica and removal of bonded phase is accelerated at high temperature, and leads to changes in retention, selectivity and peak shape, loss of column bed integrity, and contamination of product in preparative chromatography.

Because of the problems inherent in the use of silica-based chromatographic supports, a considerable amount of time and effort has been

devoted to the identification and evaluation of alternative high-performance support materials. Among these supports are cross-linked polystyrene–divinylbenzene and related supports, carbonaceous phases, calcium hydroxyapatite, alumina and many more [12]. A review of the properties and limitations of each of these supports is beyond the scope of this article. It is sufficient to note that they fall far short of fulfilling the requirements of the ideal support outlined above, and so the search goes on.

A second reason for exploring the use of different support materials is to exploit the unique surface chemistry of a particular support for a specific separation. Support chemistry is often viewed as a nuisance to be overcome, for example, by adding “masking agents” to the mobile phase, but it should be more appropriately viewed as an important variable to be manipulated in optimizing a separation. In this context, the development of new support materials with unique surface chemistry gives the chromatographer access to additional tools with which to affect a separation. Since resolution in chromatography depends much more on selectivity than on efficiency there will always exist an interest in developing new, more selective (or even “tunable” selectivity—due to unique surface chemistry) supports.

This search for chromatographic supports with

TABLE 1

COMPARISON OF SILICA, ZIRCONIA AND SYNTHETIC POLYMER SUPPORTS IN TERMS OF CHROMATOGRAPHICALLY RELEVANT PROPERTIES

++ = Very good performance; + = good performance; – = fair performance.

	Silica	Zirconia	Polymeric phases
Mechanical stability	++	++	+
High surface area	++	++	++
Control of average pore diameter	++	++	+
Control of particle diameter	++	++	++
Chemically flexible	++	+ <sup>a</sup>	+
Energetically homogeneous	–	–	+
Swelling	++	++	–
Chemical stability (acid, base)	–	++	++
Thermal stability	+	++	–

<sup>a</sup> If a method to produce a stable, monomolecular, bonded phase on zirconia were developed we would add an additional +.

improved physical and chemical properties has recently led to increased attention to transition metal oxides and related materials such as zirconium oxide, zirconium phosphate and titanium oxide [13–25]. One important reason for this interest is the remarkable mechanical, chemical and thermal stability of such materials [26–28]. The chemical stability of zirconia and zirconium phosphate has long been recognized, and has led to their use as ion-exchange materials for high-level radioactive waste treatment, recovery of fission products and high-temperature ion-exchange in the nuclear industry [29]. Literature on the use of zirconia for ion-exchange of inorganic compounds is vast [26–36]. We shall not cover this field in this review.

Zirconium oxide is known to be the only pure metal oxide which possesses four different chemical properties on its surface: acidic and basic<sup>a</sup> as well as oxidizing and reducing properties [1]. These unique properties are widely utilized in catalysis (see ref. 61 and references cited therein). The catalytic activity of zirconia makes its utility for chromatography more difficult but in liquid chromatography this activity can often be suppressed.

An enormous amount of work has been done to characterize these oxides and although the chemical stability (pH etc.) of these materials is remarkable, the amorphous precipitates and layered crystalline materials which have historically been prepared are *not at all suitable for use in HPLC*. They do not possess sufficient mechanical stability, nor have they been prepared with sufficiently high surface areas or controlled and reproducible pore geometries. Recently, spherical, porous, microparticulate zirconia and titania supports with excellent physical and mechanical properties have been prepared [24,25]. Some of the unique properties of these materials which make them attractive as chromatographic supports will be described below with a primary

focus on zirconia and modified supports prepared from zirconia.

Despite its interesting chemistry, zirconia for chromatography must fulfill certain minimum physical requirements. These requirements are quite similar both for chromatographic grade zirconia and zirconia for use in catalysis [24,37]. A well developed pore structure (excluding microporosity) is necessary both for catalysis and chromatography. Particles of uniform geometry and dispersity as well as high mechanical strength are desirable. The surface should show a BET isotherm of type IV with a type H1 hysteresis loop (IUPAC [38])<sup>a</sup>. The only exception is the catalytic activity which is highly undesirable in chromatographic materials.

## 2. PHYSICAL PROPERTIES

### 2.1. Precipitation of zirconia —dependence of physical properties on the conditions

Zirconium dioxide can be prepared by precipitation from zirconium or zirconyl salts [1] or from zirconium alkoxides [39–43]. The method of preparation strongly influences the properties of the precipitate and many examples of this can be found in the literature (e.g. ref. 1).

There is some disagreement in the literature concerning the importance of pH as a factor which can influence the crystallinity of the precipitated zirconia. Davis [44] considers pH to be the most important factor and shows that the tetragonal phase is likely to form at pH values lower than 6.5 or higher than 10.4 while in the range  $6.5 < \text{pH} < 10.4$  the monoclinic phase precipitates. Srinivasan *et al.* [45] made similar observations. However, the range of pH in which monoclinic zirconia formed was stated to be wider:  $3 < \text{pH} < 10$ . Other authors did not notice any dependence of the crystalline form on the pH [39]. Clearfield [46–48] proposed a mechanism of crystallization of zirconia depending on both pH and time. The mechanism is based on the tetrameric structure of zirconyl species found

<sup>a</sup> We will use the term acidity and basicity very often in this review. When the terms “acidity” or “basicity” are used we mean both in their broader sense, *i.e.* we mean Lewis acidity or Lewis basicity. When we refer to Brönsted acidity or basicity this will always be noted.

<sup>a</sup> The shape of isotherm and hysteresis loop will be discussed in detail in section 2.6.

in the solid state and in solution. He has shown that the slow process at extreme pH values should favor the tetragonal structure while rapid precipitation leads to amorphous precipitates or the monoclinic phase (the latter is promoted by heating). It is worth noting that tetrameric zirconium hydroxide structures contain bridged hydroxyls which will be discussed later [48–50]. We should also note that the degree of mesoporosity as well as total pore volume increases with increasing pH [37,51,52].

Zirconia can also be obtained by a thermolysis of zirconium salts. Thermal decomposition of zirconium sulphate at 1000°C leads to a mesoporous material with high (90 m<sup>2</sup>/g) surface area [53]. Decomposition of Zr(NO<sub>3</sub>)<sub>4</sub> at 500°C in the presence of H<sub>3</sub>PO<sub>4</sub> leads to amorphous, highly acidic zirconia with a specific surface area of 290 m<sup>2</sup>/g [54].

It is thus interesting to note that depending on the method of preparation and conditions of calcination, it is possible to prepare amorphous zirconia [24] or zirconia with a definite monoclinic crystallinity [30]. Generally, the precipitation of ZrO<sub>2</sub> at lower temperature leads to amorphous material while at higher temperatures crystalline phases are more likely. *It has yet to be shown whether the amorphous, tetragonal or monoclinic zirconia surfaces have different chromatographic properties.*

## 2.2. Crystallinity

Zirconia is available in four forms: amorphous, tetragonal, cubic and monoclinic. It has been known that the optical, thermal and electrical properties of the zirconia depend on its structure [55–57]; we do not doubt that zirconia's chromatographic properties will depend on its crystallinity. The crystallographic forms can change from one to another in the following way:



However, it is well known that all the above crystalline forms can be obtained at much lower temperatures, for example, by slow precipitation of hydrous zirconia and refluxing the slurry in

mother liquid one obtains the monoclinic material [46]. Cubic zirconia can be obtained similarly [46]. Amorphous precipitates usually transform to the metastable tetragonal phase upon thermal treatment and then convert to the monoclinic phase [40]:



The transition from the amorphous to the tetragonal form usually takes place at 420–470°C. This is easily observed as a sharp exothermal “glow” peak on a differential thermal analysis (DTA) curve (see refs. 24,39 and 51 and references cited therein). The exact temperature of the glow-exotherm depends on the preparative conditions [58]. The tetragonal phase is considered metastable [39,45]. The transition from the metastable tetragonal to the monoclinic crystalline phase proceeds in a temperature range between 400 and 1000°C [39,40,59,60]. The degree of conversion depends not only on the temperature but also on the total time of the thermal treatment. As a result most studies involve the use of polymorphous materials *i.e.* the substances were partially amorphous, partially tetragonal and partially monoclinic [1,51]. X-Ray diffraction shows that even materials with definite monoclinic crystallinity have a low yet discernible amount of tetragonal phase [61]. X-Ray diffraction is usually used for estimating the relative amount of the crystalline phases. However, Raman spectra [40,37,51] and <sup>17</sup>O magic angle spinning NMR spectra also appear to be sufficiently sensitive to enable detection of crystallites even when X-ray diffraction fails [62,63]. It is also worth noting that the relative amount of monoclinic/tetragonal phase can slowly change upon aging; Guglielminotti [64] noticed the transformation of the tetragonal form to the monoclinic material over a year's time. The point of zero charge (pzc) is another property which changes upon aging [65]. Polymorphism in zirconia increases surface heterogeneity. Obviously this has some effect on its chromatographic properties [66]. According to Tanabe [1] zirconia pretreated below 700°C is primarily amorphous with small tetragonal and monoclinic regions. The transformation of tetragonal to monoclinic

zirconia can also be brought about by pressure [67]. Prolonged mechanical treatment (grinding) gave a pure monoclinic phase from polymorphs containing various amounts of tetragonal and monoclinic materials [68].

### 2.2.1. Monoclinic zirconia and the origin of the surface activity

The chemical environment of zirconium and oxygen will influence their surface chemical properties and thus it is important to understand the crystal structure in some details. Monoclinic zirconia is a crystalline substance in which all zirconium atoms are heptacoordinated to oxygen atoms. This is shown in Fig. 1.

Two different kinds of oxygen atoms are present in monoclinic zirconia: tricoordinated oxygen is denoted O(1) and tetracoordinated oxygen is denoted O(2). The coordination spheres of both types of oxygens are illustrated in Figs. 2 and 3.

A stereoscopic picture of the 100 plane of monoclinic zirconia is shown in Fig. 4.

The crystalline structure of monoclinic zirconia was solved many years ago by McCullough and Trueblood [69], and Smith and Newkirk [70]. It is interesting to note that planes perpendicular to the *x* crystallographic axis are composed of sequential layers of oxygens (O1), zirconium

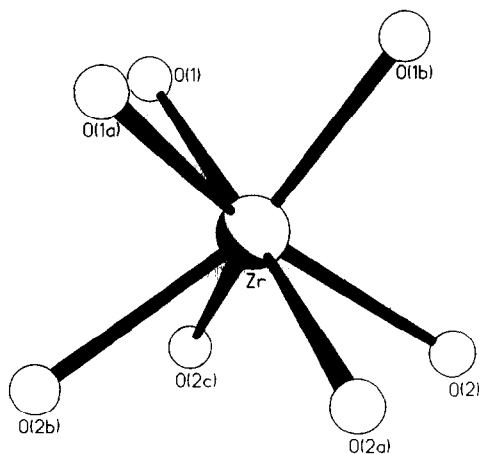


Fig. 1. Coordination sphere of zirconium atom in monoclinic zirconia. Three oxygens O1 type (O1, O1a, O1b,) and four oxygen atoms of O2 type (O2, O2a, O2b, O2c) are coordinated to each zirconium atom.

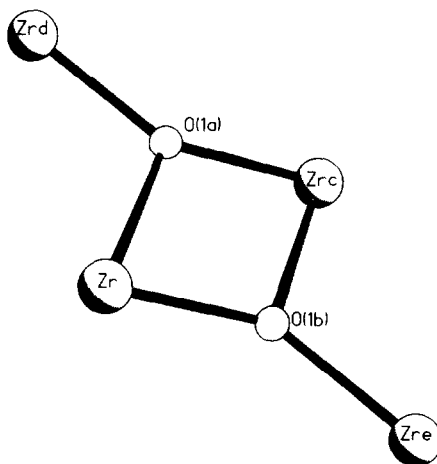


Fig. 2. Coordination sphere of O1 type oxygen atoms. Each O1 type atom is coordinated to three zirconium atoms.

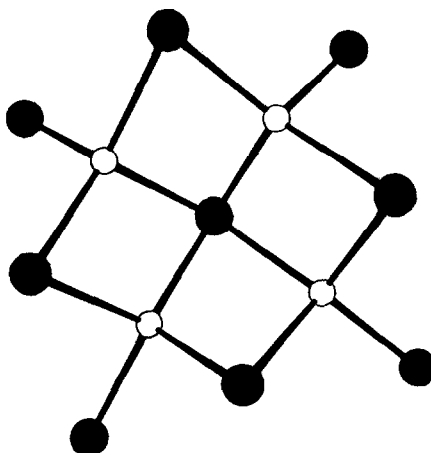


Fig. 3. Coordination sphere of O2 type oxygen atoms. Each O2 oxygen atom is coordinated to four zirconium atoms. ● = Zr; ○ = O(2).

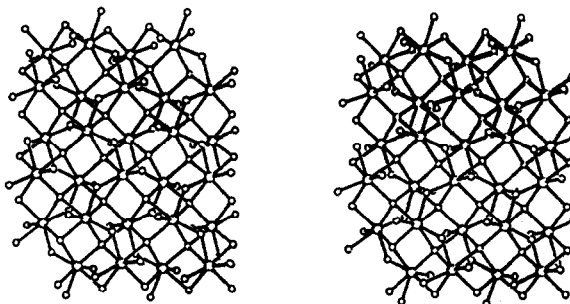


Fig. 4. Stereoscopic view of monoclinic zirconia crystal (100 plane).

atoms, oxygens (O2) and again oxygens (O1). Let us consider the structure of the zirconia surface bearing in mind this property of the oxide. First, we have to take into consideration a whole molecule of the  $ZrO_2$  —i.e. we cannot “destroy” the stoichiometry of the compound.

If we illustrate the structure of monoclinic zirconia in terms of  $ZrO_2$  molecules (Fig. 5) we will see subsequent layers of oxygen, zirconium atoms and then again oxygen. Closer inspection of the structure reveals that the oxygen atom layers inside the crystal contain twice as many oxygen atoms as does the “surface” layer. In other words Fig. 5 shows that the ratio of oxygen atoms in the surface layer to the zirconium atoms in the immediate underlayer is 1:1. Now we consider a layer of surface oxygens and a layer of zirconium atoms keeping in mind that a second layer of oxygens is below the zirconium atoms. Taking the above points into account we can identify two extreme cases: case A: the top layer is composed of O1 type oxygens or case B: the top layer is composed of O2 type oxygens.

We also assume that the atoms (Zr and O) in the surface preserve as far as possible their coordination configurations found in the bulk crystal.

In case A the zirconium atoms in layer 2 (see Fig. 5) will also be trigonally coordinated (keep

in mind that the other four coordination bonds are satisfied by the type 2 oxygens (O2) in the next plane down).

According to our assumptions, in the layer of type 1 oxygens (O1) every second oxygen atom is coordinated by two bonds to a surface zirconium atom and every second type 1 oxygen (O1) is coordinated to only a single zirconium atom. We thus observe that some coordination valencies of both oxygen and zirconium atoms are unsatisfied. In other words the surface atoms are charged. Oxygen atoms bear a negative charge while a positive charge will accumulate on the zirconium atoms. *This is the fundamental origin of the Lewis basicity and acidity of zirconium oxide* (Fig. 7).

In case B a similar analysis can be performed. Here the top layer is comprised exclusively of O2 type oxygens. In this case four coordination valences of the zirconium atoms are projected toward the top layer of oxygen. Keeping in mind that three coordination bonds of Zr are satisfied by the subsequent layer of type 1 (O1) oxygen. According to our assumptions (that is the crystalline configuration is preserved) only two of zirconium valences can be satisfied by the type 2 (O2) oxygens. We therefore see formation of Lewis acid sites on the surface, since the unsatisfied valences are equivalent to an accumulation of a positive charge on the zirconium atoms. In the next layer the type 2 (O2) oxygens can satisfy only two (of four) coordination valences and thus a negative charge will accumulate on the oxygen atoms. This is the origin of Lewis base sites on the zirconia surface (Fig. 8).

In both cases all surface zirconium atoms are Lewis acids and all oxygen atoms Lewis bases. Indeed, it has been confirmed that basic and acid sites are contiguous [71]. The average concentration of zirconium atoms on the surface is  $12.2 \mu\text{mol}/\text{m}^2$  (calculated from data in refs. 69 and 70). In reality the surface layer is usually formed in the presence of other substances like water and oxygen. When water molecules are available the surface will be covered by hydroxyls as each surface Lewis acid–base pair will likely dissociatively adsorb a water molecule. This is in agreement with general knowledge of metal oxides [72] as well as with the observed behavior of

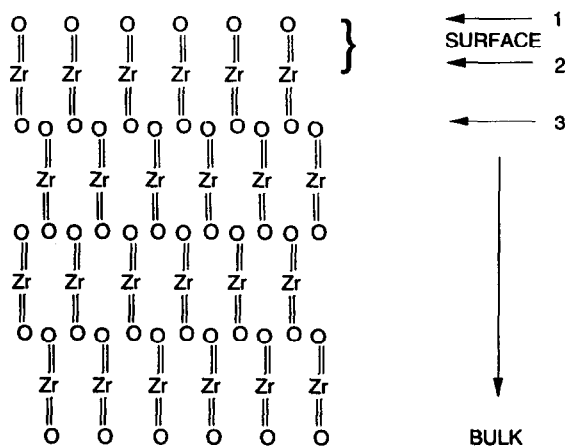


Fig. 5. Schematic view of atom layers perpendicular to  $x$  crystallographic axis (100 plane) in terms of zirconia molecules. 1 = surface layer of oxygen atoms; 2 = surface layer of zirconium atoms; 3 = layer of bulk oxygens.

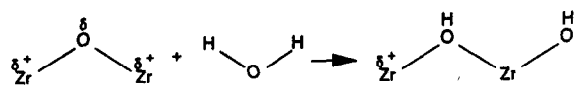


Fig. 6. Reaction of water molecule with zirconia surface.

water on thermally treated zirconia [67,73,74] (Fig. 6).

Let us note that each Zr atom bears a partial positive charge ( $\delta^+$ ) while the attached hydroxyl bears a full negative charge. This explains why surface hydroxyl groups on zirconia are Brönsted bases in contrast to these on silica which are Brönsted acids. The bridged hydroxyls will probably differ in basic strength as some of them bear partial ( $\delta^-$ ) and some of them full negative charge. Reaction of water with some acid-base pairs on zirconia surface (see Fig. 7) can lead to formation of geminal hydroxyls on the surface.

The above model leads to a surface concentration of *ca.*  $25 \mu\text{mol OH/m}^2$ . The literature reports that the surface concentration of hydroxyls is higher than  $20 \mu\text{mol OH/m}^2$  [75,76]. The surface concentrations of acidic and basic sites found in the literature vary greatly. There are substantial differences between the data from various groups. The highest results show close to  $5 \mu\text{mol}$  of Lewis acid sites/ $\text{m}^2$  and about  $4 \mu\text{mol}$  of Lewis base sites/ $\text{m}^2$ . These considerations

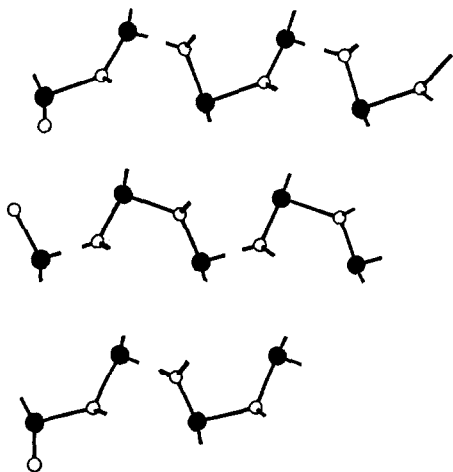


Fig. 7. Surface of zirconia (plane 100). Case A: the top layer of oxygen atoms is composed exclusively of O1 type oxygens. Note that half of the zirconium atoms have two and the other half have one unsatisfied coordination valency. The same is true for oxygen atoms. ● = Zr; ○ = O(1).

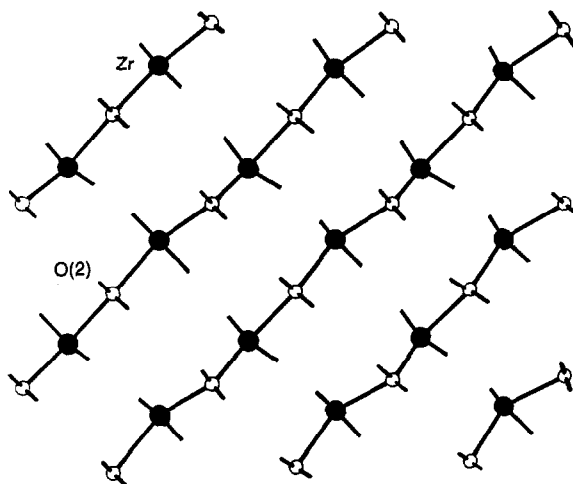


Fig. 8. Surface of zirconia (plane 100). Case B: the top layer of oxygen atoms is composed exclusively of O2 type oxygens. Note that all zirconium atoms have two coordination valencies unsatisfied. The same is true for the oxygen atoms. ● = Zr; ○ = O(1).

indicate the complexity of the zirconia surface and confirm our assumption that the surface will tend to bind any available molecule so as to satisfy its unsaturated coordination.

### 2.3. Surface area

The specific surface area of a support is generally accepted as one of its most important chromatographic parameters. The specific surface area of zirconia depends strongly on the sample's thermal history. This is shown in Fig. 9.

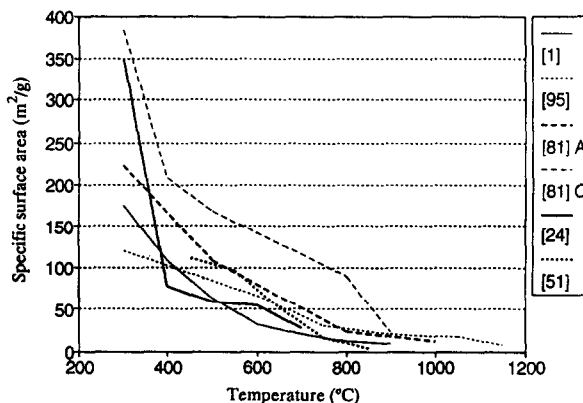


Fig. 9. The dependence of specific surface area of zirconia on temperature.



Surface area decreases sharply between 300 and 550°C. Generally, particles heated above 500°C will have a specific surface area below 100 m<sup>2</sup>/g. Two processes are responsible for the decrease in surface area: (i) microcrystallite growth and (ii) intercrystallite sintering [51].

Fig. 9 clearly shows that we cannot expect zirconia particles to have a specific surface area comparable to that of silica. Usually zirconia thermally treated below 400°C will contain micropores. However, higher-temperature treatment means lower surface area and this trend is observed essentially for all zirconias shown in Fig. 9.

The porous structure of zirconia was studied by Sharygin *et al.* [77]. Samples of zirconia subjected to heat treatment at 150–300°C were transitionally microporous, at 300–600°C transitionally macroporous and at 700–900°C macroporous adsorbents. The authors [77] estimated (applying the Dubinin equation [78]) that part of the surface area attributable to mesopores (20 to 500 Å [38]) and compared it with the total BET surface area. This is shown in Fig. 10.

A similar estimate was made by Mercera *et al.* [51] but by a different approach (the *t*-plot method of statistical thickness [79], which is based on the observation that the ratio between the adsorbed volume and the volume of a uni-molecular layer when plotted *versus* the relative pressure *p/p*<sub>0</sub> can be represented by a single curve called “the standard isotherm”. For a

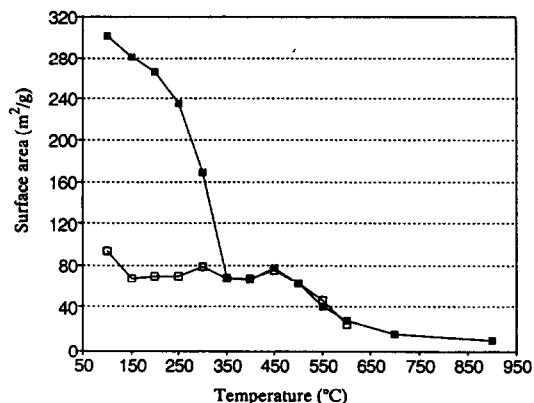


Fig. 10. Total (■) specific surface area of zirconia vs. surface area of mesopores (□) calculated by the Dubinin equation [77].

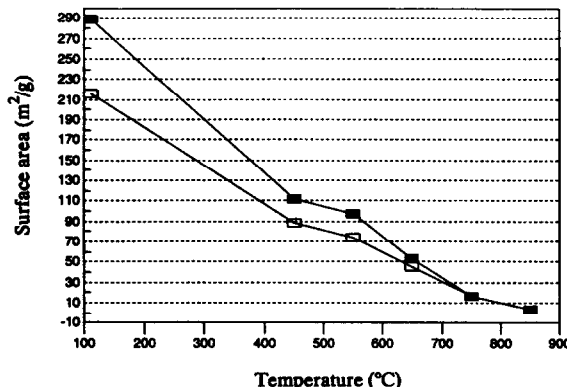


Fig. 11. Total (■) specific surface area of zirconia vs. surface area of mesopores (□) calculated from *t*-plot method [51].

review on microporosity estimation methods see ref. 242.) This is shown in Fig. 11.

The differences between the results (Figs. 10 and 11) may arise from the use of different experimental methods, or different adsorbates (Sharygin *et al.* used methanol while Mercera *et al.* nitrogen). The conclusion, however, is similar: zirconia when thermally treated only below 350–450°C will contain a considerable number of micropores.

The dependence of pore diameter on temperature as observed by four groups is shown in Fig. 12.

Despite the use of different definitions of the pore diameter (effective pore diameter [77], mean pore diameter [24] or most frequent pore

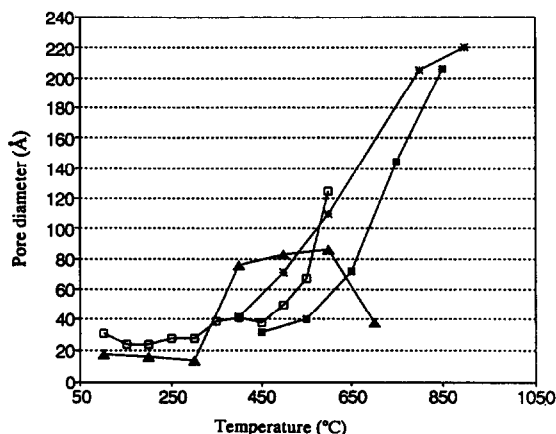


Fig. 12. Dependence of pore diameter of zirconia on thermal treatment. □ = Ref. 77; ■ = ref. 51; ▲ = ref. 24; ☆ = ref. 116.

diameter from the Barret–Joyner–Halenda (BJH) method [51] and the average pore diameter [80]) the trend observed in Fig. 12 is clear: the pore size increases with temperature.

The type of crystalline form of zirconia also seems to have an effect on the surface area. Only the tetragonal material has a surface area of 90 m<sup>2</sup>/g after treatment at 800°C [81]. However, it is known that such high specific surface areas must be due to microporosity [51]. The surface area of monoclinic zirconia seems to be more stable than that of tetragonal zirconia. This is illustrated in Fig. 13 [51,82]

Values of the specific surface area for zirconia particles used for chromatography generally fall in the ranges shown in Fig. 11, in agreement with their thermal history [19,24]. These values are generally much lower than those for chromatographic silica [4,83]; however, the density of porous zirconia is considerably higher than that of silica. The surface areas in m<sup>2</sup>/cm<sup>3</sup> of occupied bed are more comparable.

#### 2.4. Density of zirconia

The literature indicates considerable variance in the true (bulk) density of zirconia: 5.8 g/cm<sup>3</sup> [19], 5.7 g/cm<sup>3</sup> [84], 5.85 [85], 5.56 g/cm<sup>3</sup> [51], 5.89 g/cm<sup>3</sup> [86], 5.68 g/cm<sup>3</sup> [87], 5.826 g/cm<sup>3</sup> [69,88]. Similar variation in the true density is found in older sources [89]. The densities of the tetragonal form are higher: 6.10 g/cm<sup>3</sup> [51,87], 6.16 g/cm<sup>3</sup> [90] or 6.03 g/cm<sup>3</sup> [86]. Cubic zir-

conia is reported to have the highest density: 6.27 g/cm<sup>3</sup> [87]. The true density of silica is reported to be 2.2 g/cm<sup>3</sup> [4]. The apparent density of porous zirconia depends on its degree of hydration and can vary from 0.48 g/cm<sup>3</sup> to 2.33 g/cm<sup>3</sup> [84,81]. The packing density of silica varies in the range 0.2–0.8 g/cm<sup>3</sup> [4]; however, most HPLC silicas have densities in the range 0.4–0.6 g/cm<sup>3</sup> [83]. The value of the apparent density of zirconia is important for chromatography since it allows the calculation of the available surface area per unit volume of column. The apparent densities of three different zirconia samples are shown in Fig. 14.

The value of the density strongly depends on the sample's thermal history and each sample of zirconia may have its own, specific value. The apparent density of a zirconia sample increases as the sample is subjected to increasingly higher temperature treatment. Zirconia's apparent density is about 3–4 times higher than that of silica. Taking this into account, we can compare the surface area of a zirconia column to a silica column. Due to the higher packing density a 30 m<sup>2</sup>/g zirconia has a surface area equivalent to 90–120 m<sup>2</sup>/g of silica.

#### 2.5. Pore volume and porosity

The pore volume of zirconia depends strongly on its sample history. Thermal treatment at temperatures higher than 200°C gradually decreases the pore volume from 0.25 to 0.01 g/

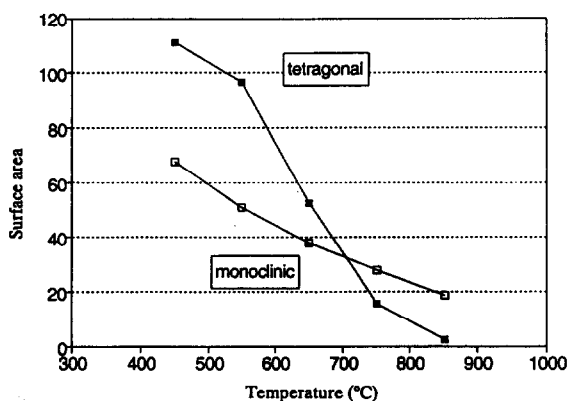


Fig. 13. Thermal stability of specific surface areas of tetragonal and monoclinic zirconias. ■ = Ref. 51; □ = ref. 82.

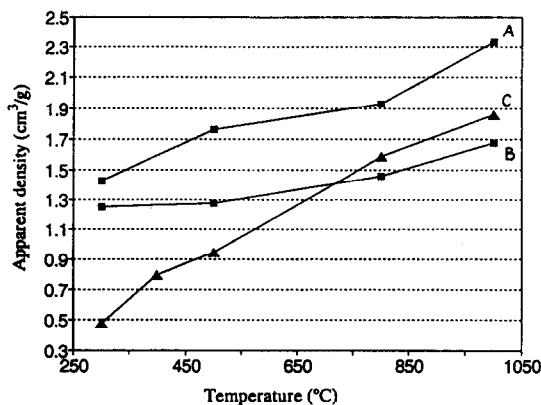


Fig. 14. Apparent density of three samples of zirconia (A [81], B [81] and C [81]) vs. thermal treatment.

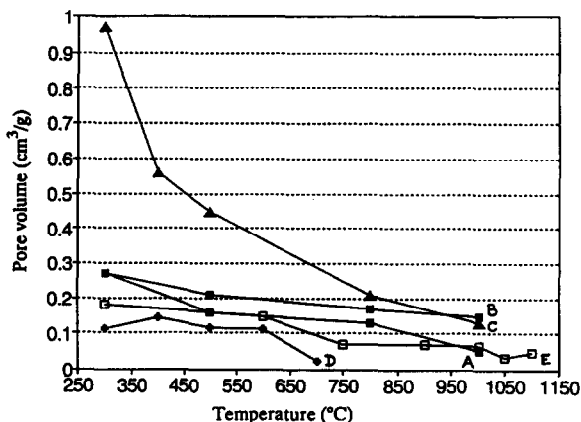


Fig. 15. Dependence of zirconia pore volume on thermal treatment (A [81], B [81], C [81], D [24], E [95]).

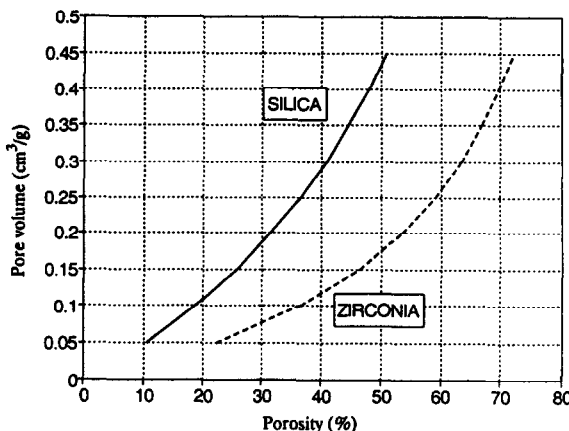


Fig. 16. Mutual dependence of pore volume and porosity for silica and zirconia.

cm<sup>3</sup>. The pore volume of various zirconias is generally much lower than that of silicas. The pore volume of sintered zirconia particles depends on the size of the microcrystallites. The dependence of zirconia pore volume on thermal treatment is illustrated in Fig. 15.

To understand why zirconia always has a smaller pore volume ( $V_p$ ) than silica, we express porosity ( $\epsilon$ ) as:

$$\epsilon = \rho V_p / (1 + \rho V_p)$$

Assuming  $\rho_{\text{zirconia}} = 5.75 \text{ g/cm}^3$  (average from all the values cited in the preceding section) and  $\rho_{\text{silica}} = 2.2 \text{ g/cm}^3$  [4], we can calculate pore volumes for the both materials at the same porosity ( $\epsilon$ ). The results are shown in Fig. 16.

As one can see, zirconia with the same porosity as silica will always have a lower pore volume than silica.

### 2.6. Pore size distribution and shape of the pores

The pore size distribution always provides much more information on the structure of the particle surface than either the mean or average pore diameter. Zirconia particles very often show a bimodal pore size distribution [91–93].

According to the IUPAC classification there are six types of isotherms and four types of hysteresis loops. They are shown in Fig. 17.

The type IV isotherm with H1 hysteresis loop is the most favorable for chromatographic purposes. The shape of the type IV isotherm is associated with capillary condensation taking place in mesopores and limiting uptake over a range of high  $p/p_0$ . The initial part of the type IV isotherm is attributed to monolayer–multilayer adsorption. This behavior is characteristic of materials comprised of agglomerates of approximately uniform spheres in a fairly regular array and having a narrow distribution of pore sizes [38]. Many porous adsorbents (e.g. inorganic oxide gels and porous glasses) tend to give type H2 loops but in such systems the distributions of pore size and shape are not well defined [38].

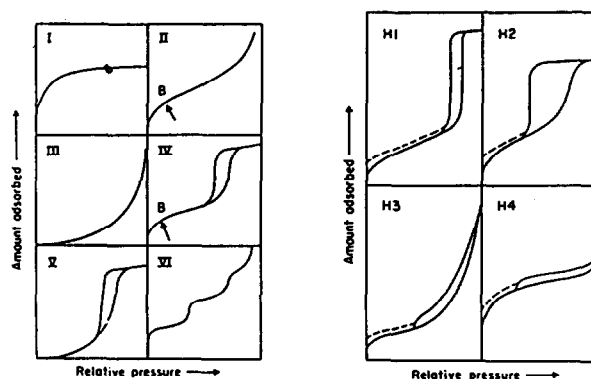


Fig. 17. Types of isotherms and types of hysteresis loops according to IUPAC classification (© 1985 IUPAC [38]).

For low temperature zirconias the pores are considered to be ink-bottle or spherical as deduced from the BET isotherm. This is unfavorable for rapid mass transfer in chromatography. Upon further treatment the pores gradually become more cylindrical [51]. Different zirconia powders can have very different adsorption isotherms and different hysteresis loops. As mentioned above, for chromatographic purposes we want a porous solid to have a type IV isotherm with a type H1 hysteresis loop. Commercial [94] and precipitated zirconias [247] often give strange type I isotherms with type H2 and H3 hysteresis loops indicative of slit-like pores. The isotherm shape improves considerably upon thermal treatment [51]. Also, use of alcohols during the preparation of the hydrogel influences the pore shape [37]. In Fig. 18 the nitrogen isotherm of a typical polymerization-induced colloid aggregation (PICA) zirconia sample [95] is shown.

The isotherm shown in Fig. 18 is of type IV with type H1 hysteresis loop. The presence of the loop in the high relative pressure range indicates mesoporosity of the solid. The pore size distribution curves (mercury porosimetry) for two PICA zirconia samples are shown in Fig. 19 [95].

The sample which was subjected to additional

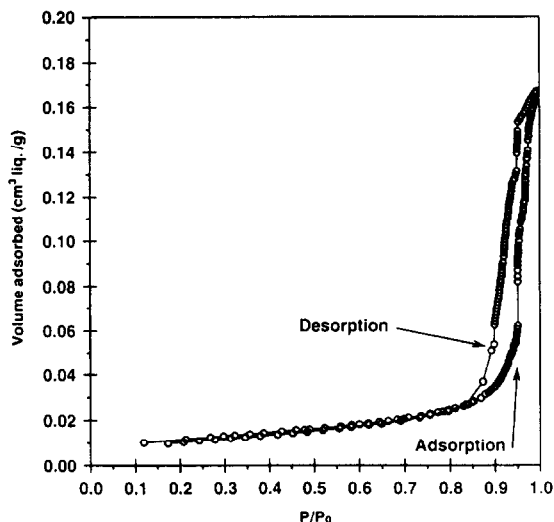


Fig. 18. Typical  $N_2$  isotherm for PICA zirconia sintered for 6 h at  $750^\circ\text{C}$  and for 3 h at  $900^\circ\text{C}$  [95].

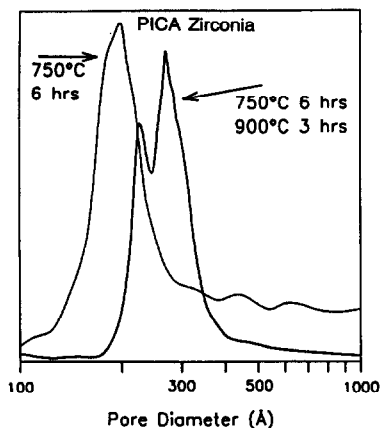


Fig. 19. Pore size distribution curves as a function of sintering conditions. (Mercury porosimetry data, [95]).

sintering at a higher temperature shows a bimodal distribution.

Two pore size distribution curves for chromatographic zirconia particles have been reported; both show unimodal pore size distribution with maximum centered at about 10 nm [19,81].

## 2.7. Mechanical strength

Particles in the 3–10  $\mu\text{m}$  range have been routinely prepared, although size classification (due to the high density of zirconia) represents a special challenge. There are no comparable data in the literature on the mechanical strength of chromatographic-grade silica, alumina and zirconia particles. It is clear that porous microparticulate zirconias can and have been prepared with the desirable physical properties associated with other high-performance inorganic supports such as silica and alumina.

The only data available on the mechanical strength of zirconia particles for chromatography show that their strength derives from microparticle sintering during thermal treatment. This is shown in Fig. 20.

Amorphous zirconia beads have been packed at pressures up to 50 MPa without cracking [24]; commercially available, non-porous zirconia particles were safely packed at 45 MPa [15]; while monoclinic zirconia particles have been packed

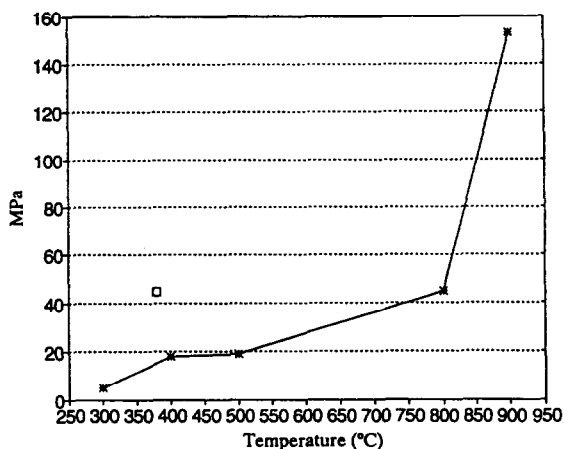


Fig. 20. Mechanical strength of zirconia particles vs. thermal treatment. \* = Ref. 81; □ = ref. 24.

at pressures up to 9000 p.s.i. (1 p.s.i. = 6894.76 Pa) *i.e.* over 60 MPa [19].

Typical mechanical stability data for a chromatographic zirconia column bed in a pressure-flow test are shown in Fig. 21.

### 2.8. Purity of zirconia

In recent years the chromatographic properties of silica have been shown to depend considerably on the presence of minute metallic impurities

(see refs. 83 and 97 and references cited therein). Zirconia is well known for its catalytic properties and it is also well known that certain additives can considerably increase its catalytic activity. For example incorporation of sulfate ions can generate so-called “superacid” sites on a  $ZrO_2$  surface while the addition of  $SiO_2$ ,  $TiO_2$ ,  $Al_2O_3$ ,  $SnO_2$ ,  $CdO$  or  $ZnO$  can considerably increase the acidity of the surface. When small amounts of silica are impregnated into the zirconia matrix they considerably increase the catalytic activity by promoting acidic properties [249].  $ZrO_2-TiO_2$  and  $ZrO_2-SnO_2$  also have significant basic properties [1]. Many zirconias are known to contain some hafnium: 1.6% Hf [41,98], 1.6%  $HfO_2$  [84] or 1.8%  $HfO_2$  [84]. Traces of Fe, Ti and Si have been reported [41,99]. Mercera *et al.* [37,51] indicated that hafnium is the main impurity in zirconia. However, traces of Cu, Fe, Ti, K and Si were also detected by X-ray fluorescence (XRF). Gimblett *et al.* [58] analyzed spectrally pure  $ZrOCl_2 \cdot 8H_2O$  and found 4 ppm (w/w) Si, 3 ppm Al, 1 ppm Ca, 1 ppm Fe, and Mg and Mn both less than 1 ppm. Holmes *et al.* [74] found 100 ppm Al, 400 ppm Ca, 40 ppm Cr, 10 ppm Cu, 3000 ppm Fe, 20 ppm Mg, 50 ppm Mn, 400 ppm Si and 10 ppm Ti. Commercially available zirconia (Degussa 137) contains 0.5% Cl and 50 ppm  $Fe_2O_3$  [99]. Three samples of zirconia were analyzed by neutron activation analysis and

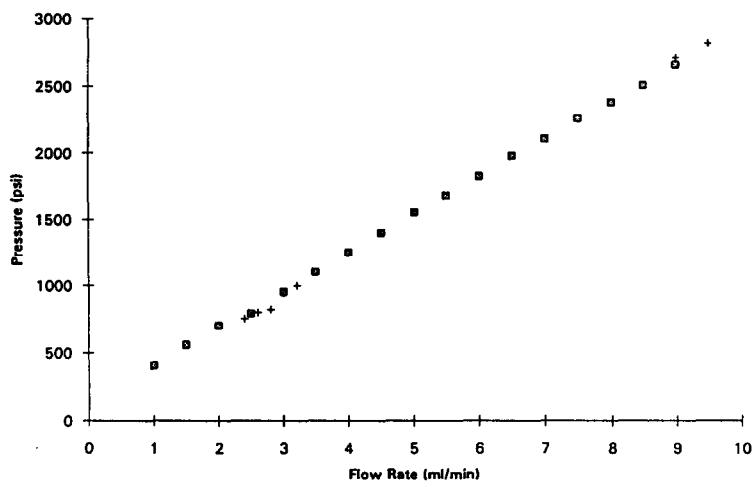


Fig. 21. Pressure-flow test of 3  $\mu m$  PICA zirconia column. Mobile phase: methanol, column  $50 \times 0.46$  cm [96]. + = Increasing flow rate; ■ = decreasing flow rate.

various amounts of Al (4.6–364 ppm), Hf (4.1–8.7 ppm), Mn (1.3–49 ppm), Th (36.4–348 ppm) and V (1.6–4.8 ppm) were found in all samples [100]. Structural impurities substantially change the  $\text{pH}_{\text{pzc}}$  of the metal oxides [101]. *It is therefore important to pay close attention to the purity of the zirconia used to prepare chromatographic materials.*

## 2.9. Commercially available zirconia powders

Commercially available zirconium oxide and titanium oxide are typically irregularly shaped, low surface area, non-porous materials. Materials of this type have been used in the evaluation of the adsorption characteristics of zirconia and

titania [13–15]. The literature reveals that a number of zirconia powders are commercially available (see Table 2).

Some commercially available samples (not specified) were found to be unsuitable for HPLC use [24]. A closer inspection of the above list confirms the conclusion of Trüdinger *et al.* [24]—zirconia particles with properties suitable for HPLC are not commercially available.

## 2.10. Requirements for and achievements in HPLC-grade zirconia technology

Porous zirconia and titania supports with many desirable properties have been prepared by sol-gel type processes [24,25]. To obtain relatively

TABLE 2  
COMMERCIAL SOURCES AND PROPERTIES OF ZIRCONIA POWDERS

Manufacturer	Type	Surface area (m <sup>2</sup> /g)	Particle size (μm)	Other data <sup>a</sup>	Ref.
Dynamit Nobel (Troisdorf, Germany)	Dynazircon	42	0.7	$D = 18 \text{ nm}$ , $V_p = 0.36 \text{ cm}^3/\text{g}$ , ( $\epsilon = 67\%$ )	84
Aldrich		1.4	—		102
Ventron		0.66	—		102
Fisher Sci.		3	2		103
Alfa-Ventron		5.8	1–3		104
Magnesium Electron	E-10	14	—	monoclinic	105
Magnesium Electron	SC-100	32	—	amorphous	105
Magnesium Electron	S-grade	9*	10 ± 3	*after hydrothermal treatment	106
Soekawa (Tokyo, Japan)		—	3		15
INVAP-Boriloch (Argentina)		5.72	0.18	monoclinic, irregular particles, 1.5 ppm F	107
Degussa	137	63.3	—		99
A.D.Mackay	Nuclear grade	23.7	—	Hf = 0.001%	94
Tosoh	TZO grade	11.8	—	$\text{pH}_{\text{iep}} = 8.2$	108
Toyo Soda (Atlanta)	TZ-O	13.5	0.200	monoclinic, $\text{pH}_{\text{iep}} = 6.5$	109
	TZ-O	—	0.05	monoclinic, $\text{pH}_{\text{pzc}} = 6.5$	110
Industrial sample (no exact source)		2.2	—	$\text{pH}_{\text{pzc}} = 4$	111, 112

<sup>a</sup>  $D$  = pore diameter;  $\epsilon$  = porosity.

uniform, small (2–25  $\mu\text{m}$ ), spherical and rigid particles, which can be used for HPLC, we can employ several different [113] methods of wet-chemical preparation of zirconia particles. Two processes are most promising: (i) sol–gel microsphere synthesis and (ii) PICA process (also called coacervation or “microencapsulation” [124,125]).

The sol–gel process can be carried out in two ways: (i) by hydrolysing zirconium compounds or (ii) by using commercially available zirconia colloids.

In the first process, the colloid must be emulsified in a water-immiscible liquid, stabilized with non-ionic surfactants and gelled by the addition of base. By adjusting the stirring velocity [24] it is possible to control the diameter of the particles. During the gelation process, colloid particles in emulsified liquid–sol droplets are converted to solid hydrogel particles. The resulting particles are subjected to a hardening process consisting of drying. The drying can be performed by: (i) conventional processes, (ii) azeotropic distillation [24] or (iii) spray-drying [92,114].

In commercially available, monoclinic [115] zirconia colloids [80,116] the size of the colloid microparticles (or core, or ultimate particles) can vary, over a relatively narrow range from 10–200 nm. The size of the colloid ultimate particles determine the final pore size of the zirconia spherule. As the water-immiscible liquid peanut oil with oleyl alcohol is commonly used [80]. Gelled spherules are separated from the reaction mixture by filtration.

The PICA process consists of the generation of: (i) a stable sol of uniformly sized colloidal particles, (ii) the addition of an organic, polymerizable and water-soluble material, (iii) initiation of polymerization of the organic material in the mixture to cause the polymerization-induced colloid aggregation into substantially spherical particles and (iv) burning off the organic material.

The PICA process produces extremely uniform zirconia particles [91]. The particle size distribution for coacervated particles of zirconia is shown in Fig. 22. For comparison the particle size distribution of coacervated silica is shown in

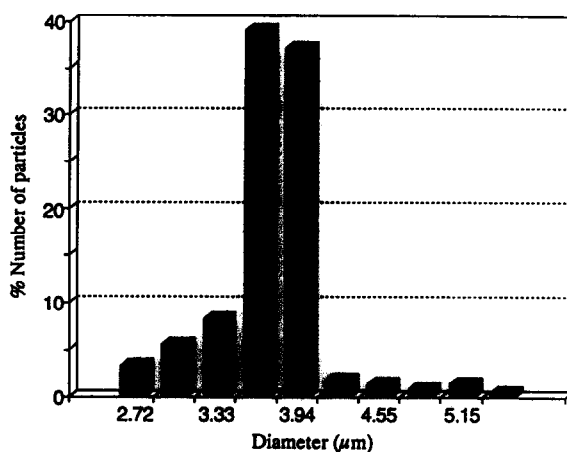


Fig. 22. Particle size distribution for coacervated zirconia [91].

Fig. 23 [117]. The average particle size of coacervated silica (Fig. 23) is slightly lower than the average particle size of coacervated zirconia (Fig. 22). It is probably easier to obtain narrower particle size fraction for larger particles. Fig. 24 shows a scanning electron microscopy micrograph of the PICA zirconia particles after sintering while Fig. 25 shows the surface of one particle.

According to one patent [118] it is possible to obtain zirconia particles with  $582 \text{ m}^2/\text{g}$  after sintering at  $900^\circ\text{C}$  or  $381 \text{ m}^2/\text{g}$  after heat treatment at  $1050^\circ\text{C}$ . In view of the preceding discus-

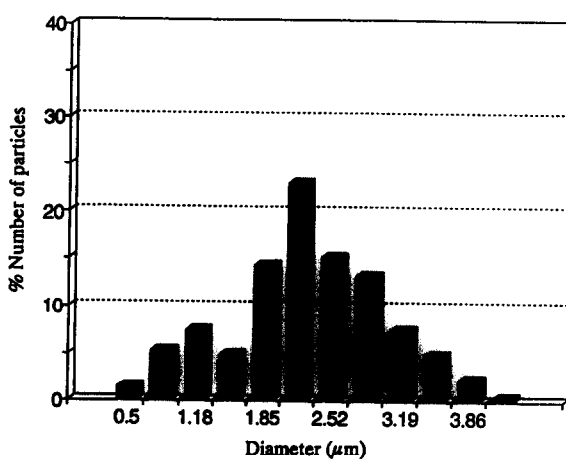


Fig. 23. Particle size distribution for PICA silica (recalculated from ref. 117).

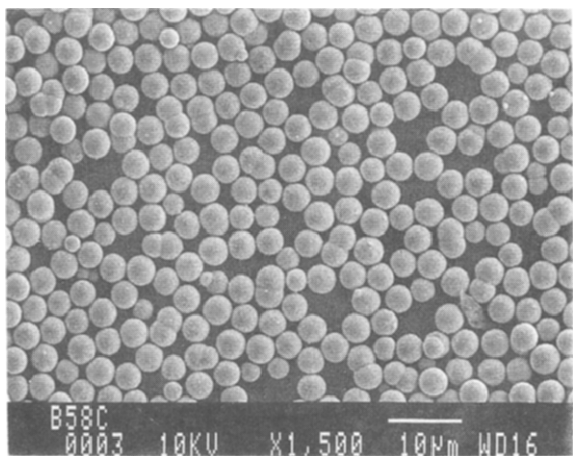


Fig. 24. SEM micrograph of coacervated zirconia particles [91].

sion concerning the surface area it is highly unlikely that such values can be realized.

Another patent claims the production of zirconia particles by simple spray-drying of sols of a zirconia colloid to which a binder is added. A binder is an active molecule which agglomerates the ultimate colloid particles and is decomposed during spray-drying. The use of zirconyl sulfate as a binder has been patented [114]. As shown below sulfates can generate superacid sites on the surface of zirconia. This will doubtless have undesirable chromatographic consequences. The patent suggests calcination at up to 800°C to



Fig. 25. SEM micrograph of the surface of a coacervated zirconia particle [91].

remove the sulfates. This is in agreement with findings of Bensitel *et al.* [119] and Escalona Platero and Peñarroya Mentrut [53]. However, according to the work of Lunin *et al.* [120] most of the sulfate is not removed until much higher temperatures 1000–1300°C.

A chemical method of producing controlled size non-porous zirconia microspheres ( $d_p < 3 \mu\text{m}$ ) has been described by Lerot *et al.* [121]. The process involves the precipitation of  $\text{ZrO}_2$  from zirconia alkoxides by addition of propanol containing water in the presence of carboxylic acids. By controlling the amount of water added to the reaction mixture and by changing the carboxylic acids from  $\text{C}_6$  to  $\text{C}_{18}$ , the authors were able to control the particle size in a very narrow and precise range from 0.4 to 2.7  $\mu\text{m}$ . However, calcination of the product at 500°C gave particles with a very low surface area of 4  $\text{m}^2/\text{g}$ . Such non-porous zirconia particles might be useful for rapid chromatographic separations of large molecules [122,123].

Non-porous particles can also be obtained by the oil emulsion procedure [24] and sintering of the resulting particles at 800°C for 6 h [126]. The particle size ranges from 1.5 to 2.8  $\mu\text{m}$  while the specific surface area is 1.4  $\text{m}^2/\text{g}$ .

In summary: samples of zirconia treated at low temperatures will have higher surface area, higher pore volume but will also have lower strength and lower apparent density. Moreover the higher surface areas and pore volumes result from the microporosity not mesoporosity as shown in Fig. 10. Lower treatment temperatures result in the presence of micropores [24,51,77]. We believe that materials for chromatographic purposes should be thermally pretreated at an absolute minimum of 400°C, to avoid micropores and to strengthen the particles. Such a material will then have a pore volume  $V_p < 0.2 \text{ cm}^3/\text{g}$  and surface area  $< 100 \text{ m}^2/\text{g}$ , while the apparent density will be 1.3–1.5  $\text{g}/\text{cm}^3$ . Such materials will have a surface area per unit bed volume comparable to that of silica with *ca.* 300  $\text{m}^2/\text{g}$ .

Oil emulsion methods [24,80,116] produce polydispersed particles which need classification before use in HPLC. PICA produces very narrow particle size distribution as shown in Fig. 22 [91]. In Table 3 we compare the physical prop-



TABLE 3

COMPARISON OF PHYSICAL PROPERTIES OF CHROMATOGRAPHIC GRADE SILICA AND ZIRCONIA PARTICLES PRODUCED BY OIL EMULSION AND COACERVATION PROCESSES

	Oil emulsion		Coacervation	
	Zirconium [24]	Zirconium [19]	Zirconium [95]	Silica [117] <sup>a</sup>
Particle size ( $\mu\text{m}$ )	6	8	5	2
Specific surface area ( $\text{m}^2/\text{g}$ )	104	61	26	60
Average pore diameter ( $\text{\AA}$ )	60	96	300	180
Specific pore volume ( $\text{cm}^3/\text{g}$ )	0.15	0.14	0.17	0.33
Particle porosity (%)	46	45	49	42

<sup>a</sup> For *n*-butylsilylated silica.

erties of chromatographic silica and zirconia produced by both methods.

Physical properties of zirconia and silica spherules produced by oil emulsion and PICA methods are similar. (However, it must be kept in mind that both zirconia materials were produced by different methods: in ref. 24 from a highly dispersed sol and in ref. 19 from monoclinic colloid particles.)

### 3. CHEMICAL PROPERTIES

#### 3.1. Chemical stability

An appropriate starting point in a consideration of zirconia as an HPLC support is its chemical stability. The remarkable stability of

zirconia can at least be partially understood based on the structure of monoclinic zirconia shown in Fig. 1. The strength of a zirconium-oxygen bond is comparable to that of a silicon-oxygen bond (see Table 4). However, in a monoclinic material each zirconium atom is bonded to seven oxygen atoms. In contrast in silica each silicon atom is only tetracoordinated to oxygen. These properties combine to make zirconia a chemically very stable material.

The chemical stability of zirconia and titania particles was measured under extreme pH conditions and compared to that of silica [15] and alumina [19]. The excellent chemical stability of zirconia was confirmed in both studies. The latter results are illustrated in Fig. 26. In this experiment, the stability of zirconium dioxide

TABLE 4

BOND ENERGIES (kcal/mol)

Bond	Metal coord. number	Energy of dissociation [85]	Bond strength [127]
Zr–O	7	180 $\pm$ 5	181.6 $\pm$ 2
Si–O	4	185 $\pm$ 7	193 $\pm$ 2.6
Ti–O	6	156	159.3 $\pm$ 1.5
Al–O	6	115 $\pm$ 2	121.3 $\pm$ 2.5

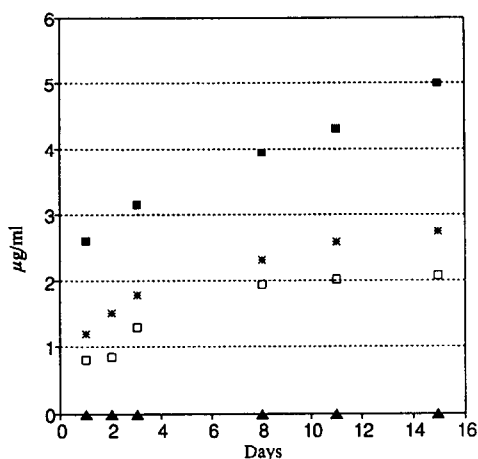


Fig. 26. Stability of zirconia and alumina over a wide pH range (replotted from ref. 19).  $\blacktriangle$  =  $\text{ZrO}_2$ , pH 1–14;  $\square$  =  $\text{Al}_2\text{O}_3$ , pH 3; \* =  $\text{Al}_2\text{O}_3$ , pH 12;  $\blacksquare$  =  $\text{Al}_2\text{O}_3$ , pH 14.

was compared to chromatographic alumina by placing the particles in a closed container and challenging them with a variety of buffers of different pH values. Despite the fact that these static conditions are far less aggressive than those used in a chromatographic stability test where the buffer is passed continuously over the surface of the particles, Fig. 26 clearly shows that alumina dissolves at pH values greater than 12 and less than 3. In contrast, no zirconia was detected at any pH from 1 to 14 using inductively coupled plasma atomic emission spectroscopy (ICP-AES) as the detection method (zirconium detection limit =  $0.03 \mu\text{g/ml}$ ). It should be noted that alumina is far less soluble in aqueous media at high pH than silica, which certainly dissolves very readily under these conditions.

The stability of zirconia under alkaline conditions has been further tested by exposing a column of zirconia to a mobile phase of 1 M sodium hydroxide at  $100^\circ\text{C}$  for 3.25 h at a flow-rate of 1 ml/min. No zirconium was detected in the column effluent after this treatment. In contrast, approximately 15% of the alumina present in a comparable column was dissolved and eluted under these extreme conditions. Clearly zirconia offers a distinct advantage relative to either silica or alumina in terms of its chemical stability [19]. According to Amphlett *et al.* [26] zirconia dissolves in acid solutions ( $> 0.1$

M); however, this was not confirmed in ref. 19. Zirconia will dissolve in HF, concentrated  $\text{H}_2\text{SO}_4$  [128] and hot, concentrated  $\text{H}_3\text{PO}_4$ . Nonetheless it has been shown that zirconia is stable under acidic conditions (HCl, pH 1). It must be pointed out that it can be dissolved in very concentrated  $\text{HNO}_3$ . The solubility in nitric acid is shown in Fig. 27. However this process is very slow [129].

### 3.2. Adsorption properties —gas—solid interface

Zirconia surfaces have been studied very thoroughly; however, materials of various origins, crystallinity and sample histories were investigated. It is therefore difficult to generalize all prior research. It is necessary to emphasize that the surface chemistry of zirconia is much more complicated than is the better known surface chemistry of silica. Fig. 28 shows the adsorption of ammonia on  $\text{SiO}_2$  (Rhone Poulenc MAS-100,  $117.5 \text{ m}^2/\text{g}$ ) and  $\text{ZrO}_2$  (Degussa 137,  $63 \text{ m}^2/\text{g}$ ) [99].

The acid site energy distribution observed for ammonia adsorption (Fig. 29) shows two highly energetic maxima on zirconia and only one, much less energetic, maxima on silica.

These figures illustrate the greater heterogeneity of the zirconia surface. In addition to ammonia, a zirconia surface is able to adsorb  $\text{CO}_2$  with high heats of adsorption [99]. On the basis of the  $\text{CO}_2$  adsorption the site energy distribu-

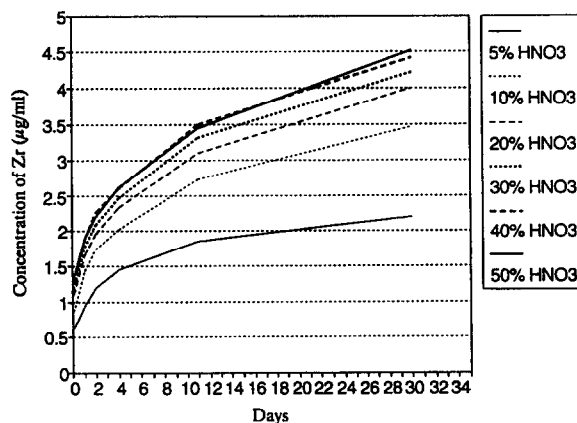


Fig. 27. Solubility of zirconia in  $\text{HNO}_3$  [130].

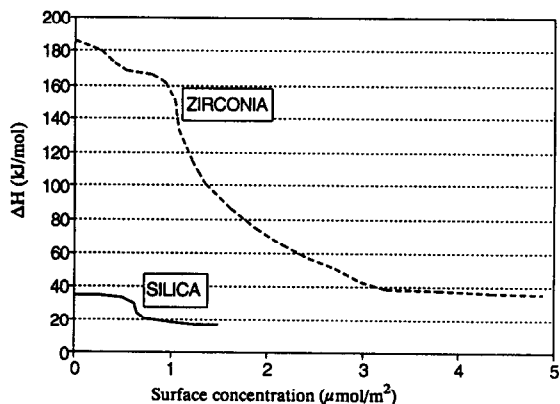


Fig. 28. Ammonia adsorption on silica and zirconia (replotted from ref. 99).

tion for basic sites was evaluated and is shown in Fig. 30 [99].

The two maxima observed for basic sites may indicate the formation of hydrogencarbonates (with basic hydroxyls) and mono- and bidentate carbonates with the basic oxygen atoms (see section 3.2.2). Another energy distribution curve for the acidic and basic sites can be found in a paper by Bibik *et al.* [131].

### 3.2.1. Water and hydroxyls

A zirconia surface at ambient conditions will carry a certain amount of both physically and chemically adsorbed water. This water can be partly removed at ambient temperature by vacuum, it significantly desorbs at 100°C and it is eventually eliminated at 150–200°C [73]. Desorp-

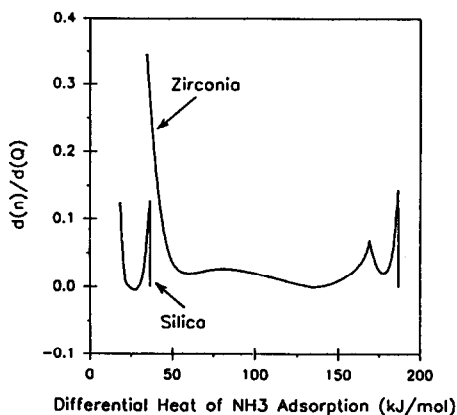


Fig. 29. Distribution of acid sites (by ammonia adsorption) on silica and zirconia (replotted from ref. 99).

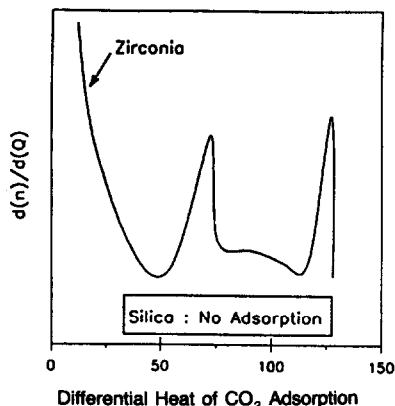


Fig. 30. Distribution of basic sites (by CO<sub>2</sub> adsorption) on silica and zirconia (replotted from ref. 99).

tion of water at 200°C is also reported in a paper by Xu *et al.* [132]. The elimination of water has been reported as being relatively easy [73]. However, it took 5 h of vacuum treatment at 500°C to get well resolved spectra of both–OH species on a zirconia surface [133,134]. The poor quality of some IR spectra [67,135] indicates the difficulties in removal of water from a zirconia surface.

When all physically adsorbed water is eliminated, IR spectra show two easily distinguished bands due to surface hydroxyls. The existence of two different surface hydroxyl groups has been confirmed in many IR studies [73,105,133]. The higher frequency band is attributed to single, isolated hydroxyl (type I; Fig. 31) while the lower frequency band is attributed to bridged hydroxyl (type II) *i.e.* hydroxyl the oxygen of which is coordinated to two zirconium atoms. These two types of hydroxyl groups are usually seen at 3770 and 3670 cm<sup>-1</sup> [133]. However, Hertl [105] observed bands at 3700 and 3760 cm<sup>-1</sup> for monoclinic zirconia but only one band

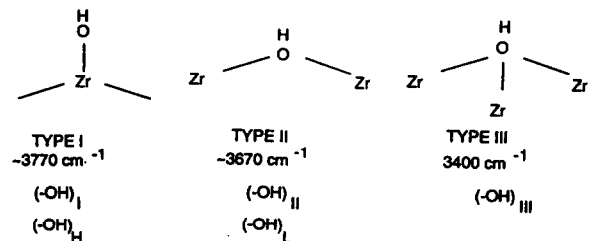


Fig. 31. Types of hydroxyl groups on zirconia surface.

at  $3659\text{ cm}^{-1}$  for amorphous zirconia. Hydroxylated tetragonal and monoclinic zirconia show spectral differences that are associated with the crystal structure and are attributed to differences in cation–anion spacings and coordination of the surface species [67]. These two crystalline forms of zirconia were also investigated by Erkelens *et al.* [135] and clearly different IR spectra were observed.

In some papers a third lower frequency–OH band is reported and it has been ascribed [133] to the presence of bridged hydroxyl groups (type III) in which the hydroxyl oxygen is bonded to three zirconium atoms. The authors emphasized that a type III hydroxyl group cannot have proton acceptor properties since both lone pairs of oxygen are engaged in bonds to metal atoms. Tret'yakov *et al.* [136] reached the same conclusion. This was supported by the observation that only the higher frequency band disappeared upon adsorption of pyridine. Taking into account the fact that solid and dissolved zirconium compounds already have bridged hydroxyls [48–50,137–139] and the evident reactivity of the lower frequency–OH band [41,98,134] we find support for the assumption that two types of bridged hydroxyls can be present on a zirconia surface: these are denoted as hydroxyls of type II and type III according to Tsyganenko *et al.*'s classification [133]. (N.B. this agrees with Tsyganenko *et al.*'s suggestions [133]). Guglielminotti [64] observed three (–OH) bands ( $3780\text{--}3760$ ;  $3680\text{--}3660$  and  $3400\text{ cm}^{-1}$ ) and assigned them as (–OH)<sub>I</sub>, (–OH)<sub>II</sub> and (–OH)<sub>III</sub>, respectively [64].

Mortera *et al.* [98] (who observed only two bands) believe that the lower frequency–OH [(–OH)<sub>L</sub>] observed at  $3670\text{--}3680\text{ cm}^{-1}$  belongs to the (–OH)<sub>H</sub> species shifted downward by H-bonding with H<sub>2</sub>O molecules. They observed a larger decrease in the (–OH)<sub>L</sub> band than in the (–OH)<sub>H</sub> band upon removal of water from the surface.

Fig. 32 shows the behavior of both (–OH) bands upon thermal treatment. As can be seen physically adsorbed water (see band at  $1630\text{ cm}^{-1}$ ) is easily removed from the surface [98]. However, Mortera *et al.*'s interpretation contradicts the conclusions of other groups

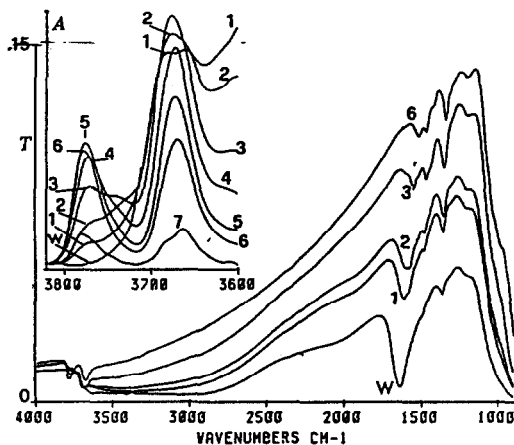


Fig. 32. IR spectrum of activation pattern of zirconia. Activation conditions: W = sample rehydrated and still in contact with 4 Torr of H<sub>2</sub>O (1 Torr = 133.322 Pa); 1 = evacuation 5 min at 300 K; 2 = evacuation 30 min at 300 K; 3 = 30 min at 410 K; 4 = 520 K; 5 = 600 K; 6 = 670 K; 7 = 770 K. From ref. 98.

[133,134,136]. According to Yamaguchi *et al.* [134] the assignment of the (–OH)<sub>L</sub> band to hydrogen bonded species is probably incorrect because this band is narrow and symmetrical. According to Lavalley *et al.* [43] some hydroxyls (of unspecified type) are involved in H-bonding. Bensitel *et al.* [41] have shown that the IR spectrum of zirconia contains two bands of  $\nu(\text{OH})$ :  $3775$  and  $3670\text{ cm}^{-1}$ . These bands are easily seen upon heating at  $200^\circ\text{C}$  under vacuum. Vacuum treatment at higher temperatures leads to a gradual decrease in the intensity of the lower frequency band while the  $3775\text{ cm}^{-1}$  band does not decrease as much. Both bands disappear at *ca.*  $600^\circ\text{C}$ . This is in agreement with the observations of Mortera *et al.* [98].

3.2.1.1. *Interactions of hydroxyl groups with alcohols.* Much attention has been paid to the interactions of alcohols with zirconia [37,38,41, 92,105,134,247] (Fig. 33). Sheifain and Makovskaya [247] investigated the role of several intermicellar liquids on the porous structure of zirconia. They found that the longer the alkyl



Fig. 33. Reaction of zirconia hydroxyl groups with alcohols.

chain of the alcohol the higher were the pore volume, the surface area and the mean pore diameter. Alcohol molecules form alkoxy groups on the surface of primary zirconia particles and consequently prevent (to some degree) the collapse of the porous structure of the hydrous zirconia upon formation of the xerogel [37]. In other words, alkoxy groups prevent formation of new Zr–O–Zr bonds during ageing. This should result in an increase in the mean pore diameter.

Also, washing ZrO<sub>2</sub> with pure ethanol after precipitation affects the properties of the calcined zirconia. The surface area, pore volume and pore radii increased significantly on washing with EtOH [37]. The BET isotherm for ethanol washed material also confirmed improvements in the pore shape. The isotherm is type IV with a H1 hysteresis loop [37,140].

Alcohols form alkoxides species with both types of hydroxyls although only the higher frequency species react with CO<sub>2</sub>. The two types of alkoxy species were said to correspond to monodentate and bridged hydroxyls [41]. This is shown in Fig. 32.

Hertl [105] noticed that hydroxyl groups of both monoclinic and tetragonal zirconia react with alcohols but the hydroxyl groups of amorphous zirconia do not. Water can displace the –OR species [105]. On the basis of their reactivity with 2-propanol Yamaguchi *et al.* [134] state that the (–OH)<sub>H</sub> species are more reactive than (–OH)<sub>L</sub> hydroxyls. Deuteration experiments also support the hypothesis that the higher frequency band is the more reactive species [105,134].

**3.2.1.2. Acidity of the surface hydroxyls.** Tret'yakov and Filimonov [141] measured the Brønsted acidity of zirconia hydroxyls by applying the method of Hair and Hertl [142]. This method is based on the measurement of the dependence of  $\Delta\nu_{\text{OH}}$  shift upon adsorption of benzene. According to them, the various –OH groups (single, bridged) present on an oxide surface have different acidities. The acidity is said to depend on the crystalline structure of the oxide. This agrees well with Tanabe *et al.*'s [143,144] hypothesis concerning the acidity of mixed oxides where coordination of both metals and various oxygens play a role in the development of surface acidity. The case of TiO<sub>2</sub> is particularly relevant, two different crystalline structures of TiO<sub>2</sub> (rutile, anatase) lead to two different surface acidities. As shown in Table 5 the pK<sub>a</sub> of an anatase hydroxyl group has been spectroscopically determined to be 0.5–2.0. The pK<sub>a</sub> value for rutile's hydroxyl group is 6.5 [141]. Similarly different acidities can be expected on the surfaces of monoclinic, tetragonal and amorphous zirconias. These were observed by Hertl [105]. In Table 5  $\Delta\nu_{\text{OH}}$  values for several oxides are compared and the relevant pK<sub>a</sub> values are given.

The data shown in Table 5 clearly indicate the very weak acidity of zirconia's hydroxyl groups. This is also confirmed by the catalytic activity of zirconia in aldol addition reactions of acetone [146,147] where the reaction is said to take place only on basic hydroxyl groups and not on surface O<sup>2-</sup> ions.

TABLE 5  
 $\Delta\nu_{\text{OH}}$  VALUES AND pK<sub>a</sub> OF THE MOST COMMON OXIDES [141]

Oxide	$\nu_{\text{OH}}$ (cm <sup>-1</sup> )	$\Delta\nu_{\text{OH}}$ (cm <sup>-1</sup> )	pK <sub>a</sub>
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	3710	110	8.5 [145]
SiO <sub>2</sub>	3750	120 (90) <sup>a</sup>	7.0 [142]
TiO <sub>2</sub> (anatase)	3725	190	0.5–2.0
TiO <sub>2</sub> (rutile)	3735	130	6.5
ZrO <sub>2</sub> (–OH) <sub>I</sub>	3770	90 (65) <sup>a</sup>	10.5; 10.7 <sup>b</sup> /11.0 <sup>a</sup>
ZrO <sub>2</sub> (–OH) <sub>II</sub>	3670	65 (47) <sup>a</sup>	12.8 <sup>b</sup> /13.0 <sup>a</sup>

<sup>a</sup>  $\Delta\nu_{\text{OH}}$  or pK<sub>a</sub> from deuterated hydroxyls.

<sup>b</sup> Calculated from data of refs. 141 and 142.

TABLE 6  
ACIDITY OF ZIRCONIA SURFACE BY AN INDICATOR METHOD

The data in the table give the concentration of acidic sites (mmol/g) having an acidity higher than the  $pK_a$  given to the right but less than that directly above the entry. 0 and  $\pm$  = detected but not quantified; – = not detected; + = detected.

Ref.	$pK_a$ of zirconia surface species									
	+9.3	+7.2	+6.8	+4.8	+4.0	+3.3	+1.5	–3.0	–5.6	–8.2
148				–	0.28	0.06	0.06	0	–	–
149	0.36	–	–	–	0.29	0	0	0		
150			<0.19	$\pm$	–	–	–	–		
151	–	+	–	–	–	–	–	–	–	–

The acidity of zirconia surface was also estimated by an indicator method. The results are given in Table 6.

As seen in Table 6 it is very difficult to get reproducible surface properties. In other paper [143] the same group reports on a distribution of basic sites on a zirconia surface. Acidic sites were not detected.

Generally, however, zirconia surfaces are slightly basic. The overall concentration of the sites calculated for a sample of  $ZrO_2$  [148] is  $5.56 \mu\text{mol}/\text{m}^2$ . This is the only sample which confirms the existence of adsorption centers with  $pK_a > 9.3$  which supports the observations of Tret'yakov and Filimonov [141] shown in Table 5. The values taken from ref. 149 can be recalculated to give  $6.05 \mu\text{mol}/\text{m}^2$  of sites with  $pK_a = 4.0$  and  $7.51 \mu\text{mol}/\text{m}^2$  of sites with  $pK_a > 9.1$ .

The higher reactivity of isolated hydroxyl groups was also observed by Tanabe and co-workers [1,134]. The isolated hydroxyl groups were selectively and irreversibly chlorinated (probably—as no adsorption product of chloroform was detected) by  $CHCl_3$  while the bridged hydroxyl groups were not. Similar chlorination results were observed with  $CCl_4$  [152]. This process was most likely responsible for the lack of elution of chloroform, dichloromethane and carbon tetrachloride in gas chromatography on zirconia particles [245]. It should be mentioned that the reaction with  $CHCl_3$  changes considerably the properties (catalytic activity, basicity) of zirconia [154].

Both–OH species are completely eliminated at

about  $600^\circ\text{C}$  [41,73] or, alternatively, according to Tret'akov *et al.* [136] at  $750^\circ\text{C}$ . Upon adsorption of water the higher frequency–OH band disappears. This supports the assumption that the free hydroxyls are engaged in H-bonding with water molecules [136]. On a dehydroxylated surface, both species (isolated and bridged) can interact with adsorbed molecules. This indicates that they are not H-bonded but are free [136]. However, according to Hertl [105], hydroxyls on tetragonal and amorphous phases are at least partly engaged in mutual H-bonding.

3.2.1.3. *Elimination of coordinatively bonded water.* Elimination of water (coordinatively bonded) and the condensation of hydroxyls leads to the development of Lewis surface acidity which first appears after activation at  $T \geq 130^\circ\text{C}$  [73].

Rehydration of the zirconia surface proceeds by dissociative adsorption of water molecules. The heat of adsorption for this process is *ca.* 180 kJ/mol [73], which is in the range for dissociative adsorption of water (250–150 kJ/mol [153,246]). Holmes and co-workers [67,74] also indicated that a considerable part of the interaction of water with dehydrated zirconia is due to a chemical process with a very high  $\Delta H$  value. Intermediate values correspond to irreversible molecular adsorption at  $Zr_{\text{cus}}^{4+}$  sites (cus = coordinatively unsaturated site) ( $120 < \Delta H < 90$  kJ/mol) and to H-bonded  $H_2O$  molecules in the first hydrated layer ( $90 < \Delta H < 50$  kJ/mol) [73,246]. Next is the physical adsorption of water with a heat of adsorption of *ca.* 44 kJ/mol (heat

of liquefaction). The  $\text{ZrO}_2$  surface can adsorb about  $6.6 \mu\text{mol H}_2\text{O}/\text{m}^2$  but only about 55% of that is adsorbed irreversibly (at room temperature). However only  $2.4 \mu\text{mol H}_2\text{O}/\text{m}^2$  are needed to completely eliminate all adsorption of CO. (Note: CO is commonly used as an indicator of Lewis acid sites.) The number of Lewis acid centers revealed by CO adsorption is about  $0.65 \mu\text{mol}/\text{m}^2$  [73,153]. This means that four molecules of water are necessary to block one CO adsorption center. The dehydration process involves, from the very beginning, some  $\sigma$ -coordination of undissociated water molecules irreversibly held at room temperatures [153]. It must be emphasized that the process of rehydration of a zirconia surface is very different from the process of dehydration [153,155]. The differences between dehydration and rehydration are shown in dehydration and rehydration IR spectra (Figs. 34 and 35).

The very complex nature of zirconia rehydration was also noted by Holmes *et al.* [94]. According to them, zirconia irreversibly binds  $11.3 \mu\text{mol H}_2\text{O}/\text{m}^2$  at  $25^\circ\text{C}$ . At  $300$  and  $400^\circ\text{C}$  zirconia adsorbs  $1.35 \text{ mg H}_2\text{O}/\text{g}$ , which is equal to  $6 \mu\text{mol OH}/\text{m}^2$ . At these temperatures, however, zirconia is not fully dehydroxylated and the surface concentration of hydroxyls may

be higher than the numbers reported. Orto *et al.* [73] have shown that the surface Lewis acidity develops by removal of hydroxyls and not by removal of water from the surface. This is illustrated in Fig. 36.

All of the discrepancies between various observations can probably be explained by the use of different zirconias, with varying degrees of crystallinity, various contents of tetragonal/monoclinic phase resulting from various methods of synthesis and different thermal histories. This, however, indicates a need for a well defined material.

### 3.2.2. Carbon dioxide adsorption on the zirconia surface

Zirconia is known to form carbonate complexes with carbon dioxide upon exposure to ambient atmosphere. These complexes are very strong and thermally stable. Morterra *et al.* [98] reported that all commercially available zirconias were heavily loaded with carbonates, not only at the surface but also in bulk, due to  $\text{CO}_2$  molecules that are trapped during the sintering process. Small amounts of such carbonates can even resist thermal treatment at  $400^\circ\text{C}$  [98] or  $300^\circ\text{C}$  [58]. Guglielminotti [64] could not eliminate many of the IR bands between  $1600$  and  $1000 \text{ cm}^{-1}$  even

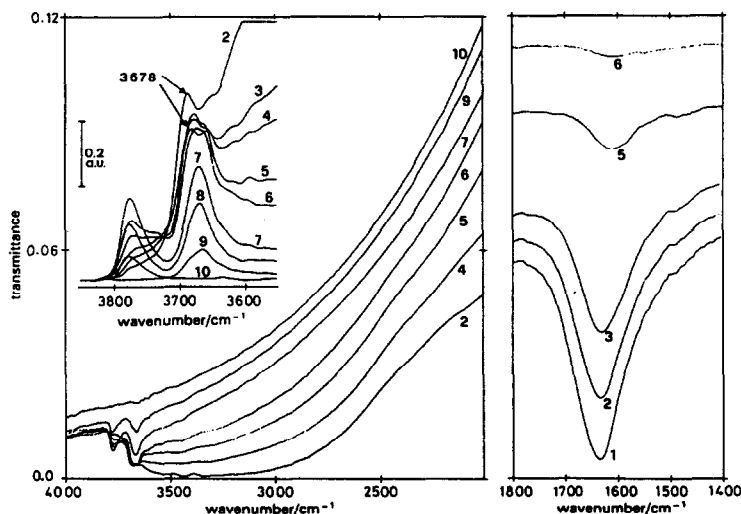


Fig. 34. IR spectra of the dehydration pattern of zirconia in the  $\nu_{\text{OH}}$  and  $\delta_{\text{HOH}}$  spectral regions. Conditions: 1 = in equilibrium with 3 Torr  $\text{H}_2\text{O}$ ; 2–4 = evacuated at room temperature for 2, 15 and 75 min, respectively; 5–10 = activated at  $100$ ,  $200$ ,  $300$ ,  $400$ ,  $500$  and  $600^\circ\text{C}$ , respectively. From ref. 155.

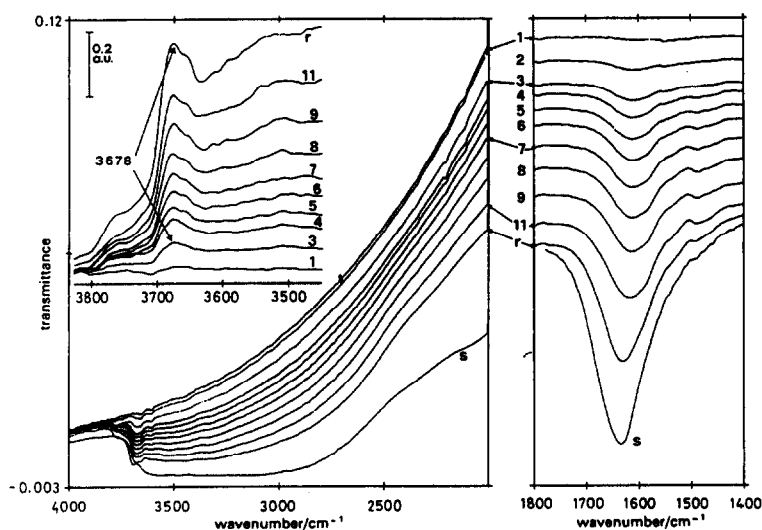


Fig. 35. IR spectra of the dehydration pattern of zirconia in the  $\nu_{\text{OH}}$  and  $\delta_{\text{HOH}}$  spectral regions. Curves: 1–11 = after admittance of successively small doses of water vapor (equilibrium  $p_{\text{H}_2\text{O}} = 0$  up to curve 9, and then  $< 10^{-1}$  Torr); s = saturated with  $\text{H}_2\text{O}$  and still in equilibrium with 4 Torr  $\text{H}_2\text{O}$ ; r = as in curve s after evacuation at room temperature for 110 min. From ref. 155.

by treatment at  $550^\circ\text{C}$ . Xu *et al.* [132] applied thermal treatment at  $600^\circ\text{C}$  for 3 h to remove carbonates from the surface of zirconia. Formation of carbonates was also noted for zirconia samples in equilibrium with water [98]. The

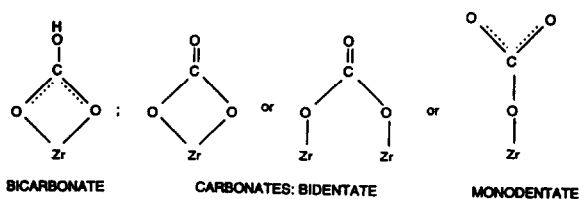


Fig. 37. Carbonate species on zirconia surface.

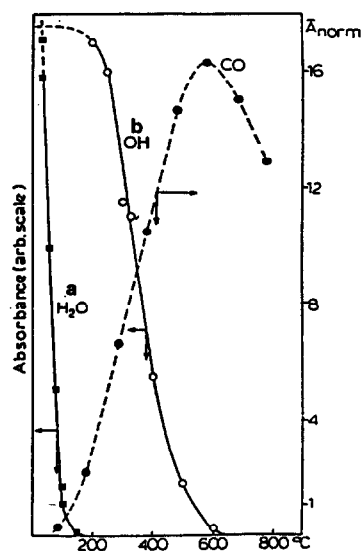


Fig. 36. Development of Lewis acidity by thermal removal of hydroxyls from zirconia surface. a = Absorbance of coordinated molecular water, b = absorbance of  $(-\text{OH})_{\text{H}}$  group, CO = absorbance of adsorbed CO. Reprinted from ref. 73.

various carbonate species that exist on a zirconia surface are depicted in Fig. 37.

The literature suggests that carbon dioxide can chemisorb on the zirconia surface in two ways: (1) at basic sites  $>\text{B}$ :  $\text{CO}_2$  (Fig. 38) and (2) at acidic sites  $>\text{A}$ :  $\text{O}=\text{C}=\text{O}$  (Fig. 39).

This property of zirconia is very important for

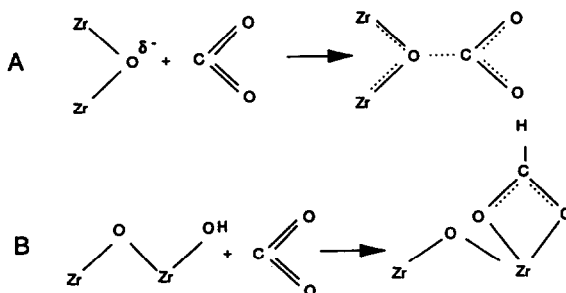


Fig. 38. Adsorption of carbon dioxide at basic sites.



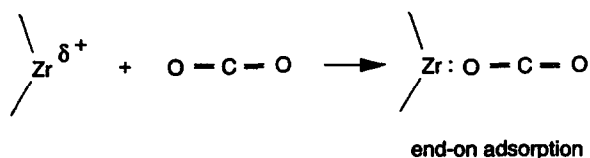


Fig. 39. Adsorption of CO<sub>2</sub> at Lewis acid site (end-on adsorption).

chromatography. Mobile phases must be free of CO<sub>2</sub> as reported by Rigney [243] and Blackwell and Carr [16–18]. The affinity of a zirconia surface for carbon dioxide and carbonates extends also to carboxylic acids which are strongly retained by the surface.

In fact CO<sub>2</sub> is often used in catalysis studies as an indicator of basic sites on the catalyst's surface [156]. The end-on surface adsorption of CO<sub>2</sub> can be used as a sensitive probe of Lewis acid sites [157]. Carbon dioxide linearly chemisorbs on a zirconia surface and gives an IR band located at 2343 cm<sup>-1</sup> which moves to higher frequencies for samples activated at higher temperatures [157]. If water is present in the system, the end-on coordination does not take place [158]. Adsorption of carbon dioxide was studied in details by Morterra and co-workers [98,153,157,158]. They have shown that three kinds of Lewis acid centers on the zirconia surface are capable of linearly chemisorbing CO<sub>2</sub>. This heterogeneity of Zr<sup>4+</sup> was also confirmed by Guglielminotti [64].

The formation of carbonates upon adsorption of carbon dioxide is thought to occur on the basic sites. However, the mechanism of the hydrogencarbonate formation proposed by Morterra and Orio [158] involves a Lewis acid site

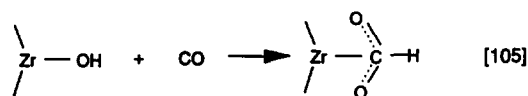


Fig. 40. Formation of formates on zirconia surface upon adsorption of carbon monoxide.

(according to them, a cation–anion pair Zr<sup>+</sup>–OH<sup>-</sup>). The hydrogencarbonates which form at the surface of highly hydrated zirconia are easily eliminated *in vacuo* at temperatures 100–150°C [155]. The desorption of bidentates gradually frees the coordinatively unsaturated surface sites whereas monodentates still present after evacuation at 300°C have almost no effect at all on adsorption of CO (*i.e.* they do not block Lewis acid sites) [155]. The papers of Morterra and co-workers do not give quantitative information on adsorption. Tanabe and co-workers [1,154] reported that 2.5–4 μmol CO<sub>2</sub>/m<sup>2</sup> adsorbed on a zirconia surface, a similar value was observed by Wang *et al.* [149]. These results are used as a measure of the basicity of a zirconia surface [1,149,154]. In view of the papers by Morterra and co-workers, these results must reflect the concentrations of both acidic and basic sites. End-on adsorbed CO<sub>2</sub> can be almost entirely removed by room temperature vacuum treatment [64,158]. However, some end-on adsorbed CO<sub>2</sub> can withstand this treatment [158]. Traces of linearly adsorbed CO<sub>2</sub> after treatment at 100°C under vacuum are evident by IR spectroscopy [159].

Adsorption of carbon dioxide generates many carbonate species on the zirconia surface. It is again worth noting that there are substantial differences between monoclinic, tetragonal and amorphous zirconia [105]. CO<sub>2</sub> adsorption also proceeds on zirconium alkoxide surfaces to form methyl carbonates [41]. A mechanism for this reaction was proposed by Tsyganenko and Trusov [160]. Reaction of carbon dioxide with a zirconia surface were also studied by others [136,104,159,161]. CO<sub>2</sub> also adsorbs on TiO<sub>2</sub> surface; however, the adsorption seems to be much weaker than that on zirconia [162].

### 3.2.3. Carbon monoxide adsorption

CO interacts with exposed coordinatively unsaturated surface cations via σ-coordination. This process is used for characterizing the surface Lewis acidity [153]. According to Morterra and co-workers [98,153,163] there are two kinds of Lewis acid sites on a zirconia surface. These sites were described as two classes of Zr<sup>4+</sup> ions, one likely belonging to flat (low index) faces and

the other exposed on high index planes. CO adsorption give rise to two closely overlapping IR bands located at 2182 and 2192  $\text{cm}^{-1}$ . The complex nature of the end-on adsorption of CO on zirconia was also noticed by Guglielminotti [64]. The chemisorbed CO can be easily removed by vacuum treatment at room temperature [64].

Hertl [105] observed a substantial difference in the adsorption of CO on amorphous, tetragonal and monoclinic zirconias. The tetragonal and monoclinic forms were able to make formates upon adsorption of CO while no formates were detected on amorphous zirconia (Fig. 41).

Kondo *et al.* [159] observed a terminal CO band at 2193  $\text{cm}^{-1}$ . Formate bands were also noted by He and Ekerdt [104] upon adsorption of CO on low surface area, monoclinic zirconia. Silver *et al.* [248] found that the adsorption of CO on zirconia depends on the time and temperature of thermal treatment. The surface concentrations of adsorbed CO were in the range 0.51–3.19  $\mu\text{mol}/\text{m}^2$ .

$\text{Zr}^{3+}$  surface centers were detected on zirconia surfaces by EPR and their existence was confirmed by IR [64,164]. Previously the signals were ascribed to  $\text{Zr}^{3+}$  ions located in the bulk of the material [165].

### 3.2.4. Bases: ammonia and pyridine

Ammonia and pyridine are often use as adsorbates to detect acid adsorption sites on surfaces.

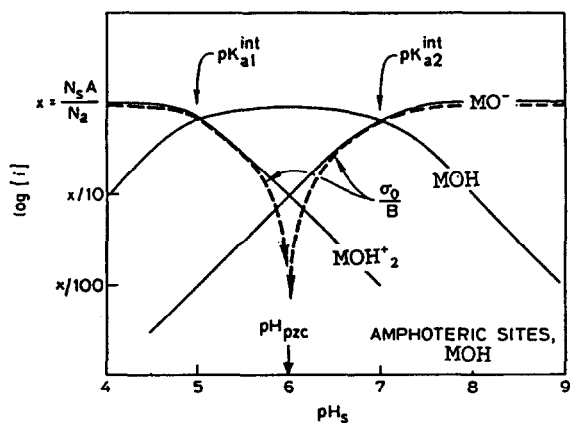


Fig. 41. Variation of charged and uncharged species concentration with the surface pH ( $\text{pH}_s$ ) (after ref. 178).

Adsorption of ammonia on the oxide surface can be very complex since  $\text{NH}_3$  can be retained on the surface in many ways: (i) through hydrogen bonding of the surface hydroxyl bond to nitrogen of ammonia, (ii) formation of  $\text{NH}_4^+$  ion, (iii) hydrogen bonding via one of the  $\text{NH}_3$  hydrogen atoms to a surface oxygen (or oxygen of a surface hydroxyl), (iv) coordination to an electron-deficient metal atom (Lewis acid site) and (v) dissociative adsorption with formation of  $\text{M}-\text{NH}_2$  and a surface hydroxyl. All of these features of  $\text{NH}_3$  adsorption are discussed in detail elsewhere [66,99].

Adsorption of ammonia on  $\text{ZrO}_2$  was first examined by Tsyganenko *et al.* [66]. They noted that the 1190  $\text{cm}^{-1}$  band ( $\delta_s$  vibration) shifts to 1230  $\text{cm}^{-1}$  upon desorption of ammonia. This indicated the presence of Lewis acid sites of various strengths on the surface. They also noticed that the position of the band depends on the method of sample preparation which is related to the polymorphous properties of zirconia. Dissociative adsorption of  $\text{NH}_3$  was observed, but the formation of  $\text{NH}_4^+$  was not. Similar surface behavior was noted by Yamaguchi *et al.* [134]. Temperature programmed desorption (TPD) profiles of  $\text{NH}_3$  indicate that desorption of  $\text{NH}_3$  molecules proceeds between room temperature and 500°C with a maximum at about 200°C [71]. Dual adsorption experiments carried out with  $\text{CO}_2$  and  $\text{NH}_3$  led to the conclusion that although independent sites are responsible for the adsorption of  $\text{CO}_2$  and  $\text{NH}_3$  some sites are in close proximity [71].

Hertl [105] observed that  $\text{NH}_3$  adsorbs on Lewis acid sites on all three forms (monoclinic, tetragonal and amorphous). Very weak bands due to the presence of  $\text{NH}_4^+$  were also observed. Dissociative adsorption of  $\text{NH}_3$  was observed on tetragonal zirconia. Hertl also determined the amounts of ammonia adsorbed on the surface of monoclinic (1.15  $\mu\text{mol}/\text{m}^2$ ) and tetragonal (0.76  $\mu\text{mol}/\text{m}^2$ ) zirconia and considered the numbers as a measure of the “Lewis acid site concentration”.

The heterogeneity of the Lewis acid sites was also confirmed by Auroux and Gervasini [99,166] who measured the differential heats of adsorp-

tion of ammonia. Two kinds of strong adsorption sites were found with strengths of over 150 kJ/mol. The total amount of  $\text{NH}_3$  adsorbed on the surface was  $5 \mu\text{mol NH}_3/\text{m}^2$  [166] which is considerably higher than the values found by Hertl [105].

Pyridine adsorption has also been used to study the acidity of metal oxides. The complexity of its adsorption is discussed by Morterra and Cerrato [167]. As with  $\text{NH}_3$ , pyridine may be H-bonded to surface hydroxyls, coordinatively complexed with Lewis sites or may form pyridinium  $\text{PyH}^+$  ion when it interacts with Brønsted acid sites. Tret'yakov *et al.* [136] noticed that pyridine interacts with  $(-\text{OH})_{\text{H}}$  species but not with  $(-\text{OH})_{\text{L}}$ . Bands due to pyridine adsorbed on Lewis sites were also found and their positions indicated that the strength of the sites is lower than that of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . The maximum amount of adsorbed pyridine on  $\text{ZrO}_2$  activated at  $400^\circ\text{C}$  found by Nakano *et al.* [154] was very low:  $0.04 \mu\text{mol}/\text{m}^2$ . Bensitel *et al.* [42] in accord with ref. 136 did not observe pyridinium ion on a  $\text{ZrO}_2$  surface. Their quantitative results are much higher than the values given by Nakano *et al.* [154]. They found that 1.0, 0.5 and  $0.13 \mu\text{mol Py}/\text{m}^2$  adsorbed after evacuation at 100, 200 and  $300^\circ\text{C}$ , respectively. Hertl [105], in addition to the bands due to coordinatively adsorbed pyridine, also observed a small band of  $\text{PyH}^+$  which indicated the presence of Brønsted acid sites. The heterogeneity of Lewis sites was also noticed by Morterra and Cerrato [167]. Pyridine adsorbs from cyclohexane solution to give a surface concentration of  $<1 \mu\text{mol}/\text{m}^2$ . Under the same conditions benzylamine adsorbs to give a coverage of more than  $3 \mu\text{mol}/\text{m}^2$  [108].

### 3.3. Surface concentration of acid and base adsorption sites in gas–solid systems

Generally the above gas–solid adsorption studies give the impression that only a rather small fraction of the zirconium ions exposed on the surface exhibit Lewis acid properties. This may be due to the use of very soft Lewis bases in these studies. These species are only able to adsorb on the strongest Lewis acid sites. Par-

ticularly low surface concentrations of Lewis acid sites are observed when CO is used as the probe. But even when stronger Lewis bases such as pyridine and ammonia are used the number of Lewis acid sites detected is still very low (Table 7). The results are not fully comparable since zirconias with various crystallinities were used, various thermal histories and various temperatures of measurement.

The exchange capacity of hydrous zirconia is 1–2 mequiv./g of  $\text{ZrO}_2$ . This value corresponds to 1–2 hydroxyl groups on eight zirconium atoms. However no surface area was provided [170].

Basicity is assessed mainly by the extent of  $\text{CO}_2$  adsorption, however, X-ray photoelectron spectroscopy and catalytic activity in the selective dehydration of 2-alcohols to 1-olefins have also been proposed as measures of the basicity of surface oxygen atoms [143,171]. The O1s binding energy in the range 529–530.5 eV was said to be characteristic of basic surface oxygen. O1s binding energy for zirconia is reported to be 529.8 eV [172,173]. In contrast O1s binding energies for alumina and silica are 531.8 and 533.1 eV, respectively [171]. Basic oxides selectively dehydrate 2-alcohols to 1-olefins. Zirconia shows a selectivity of over 90% in such reaction while alumina produces mainly 2-olefins [1].

There are also questions of a more general nature. For example,  $\text{NH}_3$  has a tendency to dissociate and adsorb on both acidic and basic sites [143]. According to Morterra's mechanism of hydrogencarbonate formation upon  $\text{CO}_2$  adsorption it proceeds on acidic (coordinatively unsaturated site) Lewis sites, however, basic hydroxyl groups take part in the reaction.  $\text{CO}_2$  is used as a basic site probe but the mechanism of carbonate species formation is not fully understood. In contrast, in liquid–solid systems, about  $12 \mu\text{mol}/\text{m}^2$  of  $\text{F}^-$  (which is very hard Lewis base) adsorb at pH 6.1 [16]. This indicates that virtually all zirconium atoms on the surface are Lewis acid sites. In liquid–solid systems (with non-polar solvents) benzoic acid can be used to detect basic sites. The concentration of the basic sites on a zirconia surface determined with a cyclohexane solution of benzoic acid was over  $5 \mu\text{mol}/\text{m}^2$  [108]. However, it is likely that the

TABLE 7

## EXPERIMENTAL SURFACE CONCENTRATIONS OF ACID AND BASE SITES IN GAS–SOLID SYSTEMS

Adsorbate	Temperature of adsorption of adsorbate (°C)	Concentration of acid sites ( $\mu\text{mol}/\text{m}^2$ )	Ref.
<i>Acid sites</i>			
Pyridine	100	0.02–0.04	1, 154
Pyridine	100	1.0	42
	200	0.5	
	300	0.13	
NH <sub>3</sub>	150	1.26 (monoclinic)	105
	150	0.76 (tetragonal)	
NH <sub>3</sub>	22	3	149
NH <sub>3</sub>	23	5	166
SO <sub>3</sub>	110	2.8–7.22	248
CO	500	0.51–3.19	
CO	room temp.	1.26 (treated at 600°C)	168
	room temp.	0.93 (treated at 800°C)	
CO		1.72	153
CO	liquid N <sub>2</sub>	3.00	169
	liquid N <sub>2</sub>	3.84	
	liquid N <sub>2</sub>	9.5	
<i>Basic sites</i>			
CO <sub>2</sub>	100	3–4	1
CO <sub>2</sub>	22	4	149
CO <sub>2</sub>	23	0.85	166
Triphenyl nitroxide	100	≈ 4 (for zirconia treated at 700°C)	1, 154

probe molecule is too bulky to detect all basic species on the surface. The Lewis acid site concentration has been estimated in liquid–solid system by an adsorption of benzylamine and pyridine. The results were over  $3 \mu\text{mol}/\text{m}^2$  and less than  $1 \mu\text{mol}/\text{m}^2$  respectively [108].

Lewis acids and bases on the surface are charged species. In gas–solid systems the species seem to be very unstable. In contrast in liquid–solid systems charged surfaces produce electrical double layers which in fact protect (stabilize) the surface charges.

The surface concentration of Lewis acid sites increase with the time and the temperature of the thermal treatment. The structures of the

adsorption sites on the zirconia surface are still not very well characterized. The literature does not even provide such important data as the surface concentration of hydroxyl groups. Based on their  $pK_a$  [141,148–151] and their catalytic activity [146,147] the surface hydroxyls were found to be basic adsorption sites. The chemical (adsorption) properties also appear to be highly dependent on the crystal form of zirconia, its method of preparation, the sample's history etc. This problem is discussed by Bolis *et al.* [168] in relation not only to two ZrO<sub>2</sub> samples but also various samples of SiO<sub>2</sub> and SiC. According to them “the surface chemistry of solids having the same (nominal) composition but different origin

may be very different". In view of the previous sections this seems to be particularly true of zirconia.

### 3.4. Zirconia as a stationary phase in gas chromatography

There are very few papers on the use of zirconia in gas chromatography. The heats of adsorption of several hydrocarbons were determined by Lapteva *et al.* [174]. They used precipitated zirconia after thermal treatment at 900°C. However, the material was microporous. Differential heats of adsorption of pentane, hexane and heptane were reported. Djordjević *et al.* [245] used monoclinic zirconia in gas chromatography. They noticed that zirconia reacts with chlorine containing C<sub>1</sub> compounds. Other chloro derivatives were relatively easily eluted from the column. Specific interactions were said to increase upon increasing the temperature at which the zirconia was pretreated. Lapteva *et al.* [175] studied the adsorption of hydrocarbons on zirconia particles but the zirconia used in that paper was poorly characterized. The reported heats of adsorption for hydrocarbons differs from those reported earlier by Djordjević *et al.* [245].

Gas chromatography can be used to characterize the zirconia surface. The utility of zirconia as a column packing for gas chromatography is minor due to its high chemical and catalytic activity.

### 3.5. Adsorption: liquid–solid interface

#### 3.5.1. Introduction

We now turn to liquid–solid zirconia interfaces. In liquid–solid systems (most of the systems examined were limited to water) zirconia surfaces contain an adsorbed water layer. As we have already seen from gas–solid studies, zirconia surfaces contain several types of adsorption sites. The coordination sites of zirconium are occupied by water, hydroxyl ions, and hydrogen ions, depending upon the pH. These sites are electropositive and exhibit properties analogous to the coordination chemistry of transition metal ions in solution. The sites can form

coordination complexes with a number of Lewis bases, particularly hard bases such as polyoxy anions (borate, sulfate, carboxylate and phosphate [72,176,177]) and fluoride [16,17,87]. Of course, a great deal of heterogeneity can exist in all of these sites because of the various geometries, surface defects and bonding types. Generally the same properties should be observed in liquid systems as seen in gas–solid interfaces. One of the striking differences (between gas–solid and liquid–solid systems) is that none of the liquid–solid systems can distinguish between the two (or even three) kinds of hydroxyls present on the surface. Another, obvious difference is the ability of zirconia to exchange ions. The surface of oxides at liquid–solid interface can be investigated by potentiometric titration, microelectrophoresis and colloid stability studies as well as by liquid chromatography. Liquid–solid equilibria differ from gas–solid equilibria in that the surface maybe charged. There are several methods of observing the accumulation of charge on the surface. These include: electrokinetic methods, conductometric titration of solids and examination of the electrical double layer of colloids. All of these methods are described by James and Parks [178]. Several catalysts were examined by Kita *et al.* [76] at the liquid–solid interface. Satisfactory correlations (between gas–solid and liquid–solid properties) were found for almost all of the oxides investigated. For zirconia, however, the results did not correlate well with those for the gas–solid interface. The amount of acid sites determined (by the titration with KOH to pH 10.5) on a ZrO<sub>2</sub> surface was equal to 12.1 μmol/m<sup>2</sup>. As they considered all species whose pK<sub>a</sub> values are less than 10.5 as acids, these results correlated quite well with those of Wang *et al.* [149] (see Table 6) where the total amount of acid was determined as 13.5 μmol/m<sup>2</sup>. However, the distribution of acidity is quite different. In ref. 76 the acid functionality had the property: 3 < pK<sub>a</sub> < 5–6. However, it must be mentioned that the pH<sub>pzc</sub> = 2.7 determined by Kita *et al.* [76] is very different from the average value of pH<sub>pzc</sub> = 6–7 (see Table 8). According to Tanabe [179], in the presence of moisture, Lewis acids convert to Brønsted acids,

TABLE 8  
VALUES OF pH FOR pzc OR iep FOR ZIRCONIA PARTICLES

pH (pzc or iep)	Method	Ref.
6.7	maximum flocculation rate	182
6–6.6	titration (5 samples)	183
4	electroosmosis	184
6.7	mobilities	185
6.7	titration	185
10	ion exchange	26,186
5.5–6.2	addition	187
12.07	calculated	188
10–11	no method specified	188
6.8	mobilities	189
6.4	titration	107
6.5	mobilities	107
6.0	addition	107
6.05	?	190
6.7	mobilities	59
8.2	titration	68
6.6	streaming potential measurements	103
8.2	commercial data	108
6.7	electrophoretic mobility	191
2.7	titration	76
4.0	titration	111
4.0	adsorption	192
5.0	mobility	110
7.5	titration	193

but hydroxyls on zirconia surfaces do not show any Brønsted acidity. Only in Hertl's work [105] were small amounts of  $\text{NH}_4^+$  and  $\text{PyH}^+$  ions noticed. We believe that the zirconia hydroxyls show very weak Brønsted acidity and also are fairly weak bases. The quantity of the hydroxyls on the zirconia surface was determined, by titration with  $\text{Zn}^{2+}$  [180], as  $21.95 \mu\text{mol}/\text{m}^2$  [76]. This is very close to the results of Randon *et al.* [75] obtained by a different method. A definite difference between gas–solid and liquid–solid interfaces is the lack of any basic site activity in the water–zirconia systems [76]. However, with non-polar solvents and benzoic acid as the probe over  $5 \mu\text{mol}$  of basic sites/ $\text{m}^2$  were detected [108].

As Davis *et al.* [181] pointed out, no comprehensive model exists which can simultaneously predict adsorption density and other surface properties. This is why liquid–solid systems

require the number of active sites on the surface to be determined by other, independent methods. Given the site density, differences between the types of hydroxyls (*i.e.* their  $\text{p}K_a$  values) can be calculated. The electrical double layer model was derived for non-porous, crystalline oxides. Thus some monoclinic zirconia powders could fulfill these requirements.

The phenomena observed in water–zirconia systems can be classified as ion and/or ligand exchange. Zirconia is known as an ion exchanger having both cation- and ion-exchange ability due to its amphoteric nature [34,36]. The cross-over coincides with the point of zero charge. It is thus of obvious interest to know the surface equilibria which govern the ion and ligand exchange as well as the exact value of the point of zero charge or the value of pH at which the ion electrophoretic mobility (iep) is equal to zero. The adsorption properties of zirconia particles (in liquid–solid systems) will thus depend on the pH of the environment.

### 3.5.2. Point of zero charge

The pzc and iep values can be measured by various methods [107] in many electrolytes provided that there is no specific adsorption of the ions on the surface [178]. In simple electrolyte systems (*e.g.*  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{KClO}_4$ ) no net specific adsorption occurs and the  $\text{pH}_{\text{pzc}}$  equals the  $\text{pH}_{\text{iep}}$  [181]. Davis *et al.* [181] pointed out that this is rather the case for “symmetrical specific adsorption” of the electrolyte cation and anion. Specific adsorption occurs if a binding mechanism, other than a coulombic one is significantly involved [72]. Regazzoni *et al.* [107], Randon *et al.* [75], Persin *et al.* [193] and Milonjić *et al.* [192] compared the  $\text{pH}_{\text{pzc}}$  values of zirconia from various sources. They vary from 2.7 to 12.07 although most of the values were found to be between 6 and 7. The data are collected in Table 8.

$\text{pH}_{\text{pzc}}$  values can be influenced by the degree of hydration of the surface and by impurities [101]. Even very low quantities of structural (built in the oxide matrix) and adsorbed (on the surface) impurities can substantially change  $\text{pH}_{\text{pzc}}$  values. Variation in isoelectric points for

TABLE 9  
 VARIATION OF  $\text{pH}_{\text{pzc}}$  UPON HYDRATION

Oxide	$\text{pH}_{\text{pzc}}$	Hydrous oxide	$\text{pH}_{\text{pzc}}$	$\Delta\text{pH}_{\text{pzc}}$	Ref.
$\text{Fe}_2\text{O}_3$	6.7	$\text{Fe}_2\text{O}_3$ (hydrous)	8.6	1.9	101
$\text{Al}_2\text{O}_3$	6.7	$\text{Al}_2\text{O}_3$ (hydrous)	9.2	2.5	101
$\text{TiO}_2$	4.7	$\text{TiO}_2$ (hydrous)	6.2	1.5	101
$\text{ZrO}_2$	8.2	$\text{ZrO}_2$ (hydrous)	6.8	-1.4	65,102

oxides and hydrous oxides are compared in Table 9.

It is interesting to note that according to refs. 65 and 102 the  $\text{pH}_{\text{pzc}}$  of zirconia changes in the opposite direction upon aging when compared to the behavior of other oxides. A gradual shift of the  $\text{pH}_{\text{pzc}}$  value from 8.2 to 6.8 for fresh and aged samples, respectively, was observed by Ardizzone and co-workers [65,102]. According to them [65] a partial dehydroxylation takes place at 800°C and a very slow rehydroxylation takes place in water to form a surface layer of  $\text{Zr}(\text{OH})_4$ . However, as emphasized in section 3.2.1 treatment at 600°C is sufficient to remove water and all hydroxyls. The slow and very complex kinetics of rehydration were also observed by several authors [94,153]. According to Ardizzone and co-workers [68,102] the measured value of the point of zero charge is pH 6.5 which is characteristic of  $\text{Zr}(\text{OH})_4$ . A similar suggestion was made by Blesa *et al.* [59]. The  $\text{ZrO}_2$  surface becomes modified in water to give a gel-like coating only a few monolayers thick. If this hypothesis is true, structures resembling those of soluble  $\text{Zr}(\text{OH})_4$  tetramers [47,50] should exist on the zirconia surface. Then the surface would likely contain a population of geminal hydroxyls. This could be confirmed by  $^{91}\text{Zr}$  cross-polarization magic angle spinning NMR [194]. This would also be in agreement with our hypothesis as to the presence of geminal hydroxyl sites on the zirconia surface (see section 3.2.1). Ardizzone *et al.* [68] reported that charge densities on zirconia treated at 200°C are much lower than those on materials fired at 800°C. However, the very high pore volumes of all materials investigated in that paper, except for that treated at 800°C zirconia, indicate a high

degree of microporosity, which is likely to influence the equilibria during titration. Stumm *et al.* [72] emphasize that surface equilibria are attained very slowly and we usually observe only metastable states. This is even more likely in the case of microporous materials. This has also obvious implications for chromatography. Slow surface equilibria would be detrimental for chromatography. It is thus important to use zirconia particles without micropores (*i.e.* sintered at temperatures assuring the removal of micropores, see Figs. 10 and 11). This also implies that crystalline, monoclinic zirconia rather than the amorphous oxide should be used. Due to the dehydroxylation of the surface during sintering *it is necessary to rehydrate (or rehydroxylate) the surface by subsequently washing it with acid and base.*

Values of the surface charge density for the 800°C treated sample correlate well with that of a monoclinic, low surface area zirconia [107]. Regazzoni *et al.* [107] measured the pzc as pH 6.0–6.5 by three different methods. They also calculated values of  $\text{p}K_{\text{a}1}^{\text{int}}$  and  $\text{p}K_{\text{a}2}^{\text{int}}$  (see Table 10) in accordance with the Davis, James, Leckie (DJL) model [181] which is in good agreement with the data given by Amphlett *et al.* [26]. Regazzoni *et al.* [107] assumed that there are about 12 sites/ $\text{nm}^2$  on the zirconia surface (*i.e.* 20  $\mu\text{mol}/\text{m}^2$ ) but offered no experimental evidence. Randon *et al.* [191] calculated a surface concentration of sites ( $N_s$ ) that can exchange protons and arrived at a value of  $N_s = 14$  sites/ $\text{nm}^2$  which is equal to 23.2  $\mu\text{mol}/\text{m}^2$  [75]. This number of sites would be possible but there would have to be one hydroxyl group on each surface zirconium atom and every bridging oxygen would have to be in the form of a bridging

TABLE 10

COMPARISON OF INTRINSIC IONIZATION CONSTANTS FOR ZIRCONIA AND OTHER OXIDE SURFACE HYDROXYL GROUPS

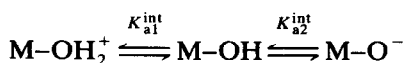
$pK_{a1}^{int}$	$pK_{a2}^{int}$	pH <sub>pzc</sub> calc. from eqn. 1	pH <sub>pzc</sub> experimental	Electrolyte	Ref.
<b>ZrO<sub>2</sub></b>					
4.2	8.6	6.4	6.4	KCl	107
4.8	10.4	7.6	7.5	water	193
4.3	9.3	6.8	7.5	NaCl	
6.2	8.3	7.25	6.7		
5.9	7.7	6.8	4.0	LiCl	192
5.8	7.2	6.5	4.0	NaCl	
5.8	6.8	6.3	4.0	KCl	
<b>Al<sub>2</sub>O<sub>3</sub></b>					
7.89 <sup>a</sup>	9.05	8.47	8.5	NaCl	178
8.50 <sup>b</sup>	9.70	9.10	9.10	NaCl	
<b>TiO<sub>2</sub></b>					
5.41	6.38	5.90	6.00	NaNO <sub>3</sub>	178
<b>SiO<sub>2</sub></b>					
1.34	4.6	3.00	3.00	KCl	178

<sup>a</sup> Data for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>b</sup> Data for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

hydroxyl group. Milonjić *et al.* [192] also examined the interfacial properties of precipitated zirconia. This is the only paper which recognizes the diversity of hydroxyls on the ZrO<sub>2</sub> surface. They interpret  $pK_{a2I}^{int}$  and  $pK_{a2II}^{int}$  values ( $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  values in Table 10) as the ionization constants of (–OH)<sub>I</sub> and (–OH)<sub>II</sub>, respectively. However, these values were calculated assuming the total capacity of zirconia surface to be equal to 5 sites/nm<sup>2</sup> (*i.e.* 8.3  $\mu$ mol/m<sup>2</sup>) [192].

### 3.5.3. Surface equilibria

Yates *et al.* [195] proposed a site binding model for metal oxides and used it as the basis for explaining the differences between silica and most other oxides. The model assumes a very simplified picture of a porous oxide surface:



where  $K_{a1}^{int}$  and  $K_{a2}^{int}$  are the intrinsic ionization constants.

Thus in the Yates model, H<sup>+</sup> and OH<sup>–</sup> are the

potential determining ions. The resulting surface charge depends on an excess of one type of charged site over the other and is a function of solution pH. The point of zero charge is the pH at which the number of positively charged species (M–OH<sub>2</sub><sup>+</sup>) is equal to the number of negatively charged species (M–O<sup>–</sup>) on the surface. As we can see the pH<sub>pzc</sub> depends on the ionization reactions and it is related to the ionization constants by the equation [178]:

$$pH_{pzc} = 0.5(pK_{a1}^{int} + pK_{a2}^{int}) \quad (1)$$

Schematic illustration of the variation of charged species concentration with the pH<sub>s</sub> for amphoteric surfaces is given in Fig. 41 [178].

Fig. 42 shows that: (i) at pH values between  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  the amount of undissociated hydroxyl groups is constant, (ii) the surface charge increase starting from the pH<sub>pzc</sub> in both acidic and basic directions and (iii) above  $pK_{a1}^{int}$  and below  $pK_{a2}^{int}$  the surface hydroxyl groups are mainly in the ionized forms.

There have been many attempts to calculate



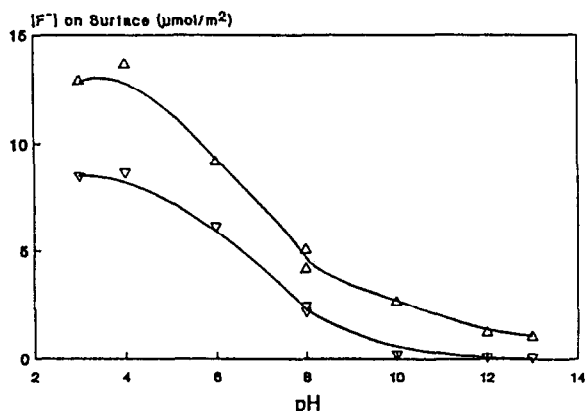


Fig. 42. Fluoride adsorption as a function of pH.  $\Delta$  = fluoride adsorption,  $\nabla$  = fluoride desorption at pH = 13. Buffers are all 0.1 M and contain 20 mM sodium fluoride except where noted. For pH = 3, 0.001 M HCl; pH = 4, acetate; pH = 6, MES; pH = 8, TAPS (top), TRIS (bottom); pH = 10, CAPS; pH = 12, 0.01 M NaOH; pH = 13, 0.1 M NaOH. From ref. 16.

the  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  values. There is also a very good correlation between the  $pH_{pzc}$  values calculated from eqn. 1 and those observed experimentally. This is shown in Table 10.

The practical meaning of the intrinsic ionization constants is that at  $pH < pK_{a1}^{int}$  zirconia will act as an anion exchanger while at  $pH > pK_{a2}^{int}$  zirconia will behave as a cation exchanger.

The intrinsic ionization and complexation constants of oxide surfaces were further investigated by Davies *et al.* [181] who modified the Yates model to include the formation of surface complexes. However, both of these theories, as we have pointed out above, require the number of adsorption sites from other, independent methods. Potentiometric titration can give some numbers [181], however, the results will depend on both the pH and the ionic strength of the solution during the measurement.

It is well known that cations and anions can adsorb specifically on the surface thus influencing the surface charge. In the case of simple electrolytes it is believed that there is no specific adsorption [178] or the adsorption of cations and anions is "symmetrical" [181]. Surface charge asymmetry may result when: (i) the inner layer capacitances of the interface for positively and negatively charged surfaces are different, (ii) the surface complexation strength of cation and

anion are unequal or (iii) the valences of the cation and anion are unequal (e.g. 2:1 or 1:2 electrolytes).

These phenomena are caused by ion exchange. Hingstone *et al.* [196] have found that some anions can adsorb to a greater extent than would be predicted from their concentration when compared to non-specifically adsorbed anions. They also noted that: (i) adsorbed anions shift the pzc toward more acidic values (the surface becomes more acidic), (ii) this is due to displacement of hydroxyl ion from the inner Helmholtz layer —*i.e.* ligand exchange, (iii) specifically adsorbed anions cannot be desorbed by a solution of non-specifically adsorbed anions (at the same pH and ionic strength), (iv) to desorb specifically adsorbed anions it is necessary to make the charge on the surface more negative than the equilibrium value at which adsorption took place and (v) the same effect is accomplished by raising the pH thus increasing the adsorption of hydroxyl ion.

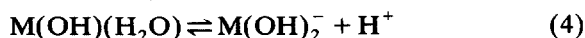
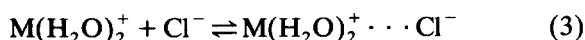
Stumm *et al.* [72] made similar observations and according to them the extent of adsorption (or surface coordination) will depend strongly on: (i) pH, (ii) the surface coordination constants, (iii) the surface charge, (iv) the type of the surface species (*i.e.* mono- or bidentate, protonated or deprotonated ligand etc.) and (v) the maximum amount of adsorption is likely to occur at about  $pH = pK_{a,HA}$  [72] in agreement with ref. 196. The dependencies listed by Stumm *et al.* [72] were confirmed in a study of the chromatography of benzoic acid derivatives on zirconia [176,177].

The study of these equilibria under static conditions is very difficult due to many limitations. Surface sites at edges, corners and faces are likely to possess different energies, not all surface sites are available due to geometric reasons and the addition of new charged groups influences the acidity of the remaining-OH groups [72]. (Similar phenomena are observed on gas-solid interfaces [1,197]).

The models of Hingstone *et al.* [196] and Stumm *et al.* [72] assume that a neutral surface site can be represented as MOH (M—metal atom of metal oxide) and ligand exchange proceeds between the  $OH^-$  and an anion. Regazzoni *et al.*

[198] argued that the metal oxide surface must contain chemisorbed (undissociated) water, the molecules of which also take part in ligand exchange. Although their discussion concerned the behavior of hematite it is most likely that the same is true of zirconia. To prove this we refer to the papers by Morterra and co-workers [73,153,155] concerning dehydration and rehydration of a zirconia surface (see section 3.2.1) where  $\sigma$ -coordination of water molecules at early stages of rehydration was proposed to explain the observed adsorption properties. As can be seen in Table 10 a silica surface is much more acidic and can behave as a cation exchanger. However, silica does not show any ligand-exchange behavior and it differs very much from the other oxides. Regazzoni and co-workers' hypothesis of ligand exchange of water molecules can explain the difference. The coordination number of a silicon atom in a silica matrix is low (4) and silicon never coordinates water molecules in its coordination sphere as do other oxides. This is probably why silica differs so much from other oxides. This would also mean that ligand exchange with coordinatively bonded water is more important than so far believed.

Based on the detailed theoretical and experimental work of Hingstone *et al.* [196], Yates *et al.* [195], Davis *et al.* [181] and Stumm *et al.* [72] and the papers of Regazzoni *et al.* concerning zirconia [107] and hematite [198] surfaces it is possible to write the most likely model for the ion- and ligand-exchange ability of zirconia. The following chemical equilibria have been used to describe the interaction of various species with the different sites on a zirconia surface [16]:



where M represents the metal oxide metal and  $\text{L}_1$  and  $\text{L}_2$  represent a Lewis base present in the eluent and a Lewis base solute, respectively. Taken together, reactions 2 and 3 account for the presence of anion-exchange sites on the zirconia surface and the retention of non-coordinating anions (denoted  $\cdots \text{X}^-$ ), such as chloride, nitrate and perchlorate. As the pH is increased, the anion-exchange capacity of the material decreases, as predicted by the shift to the left in process 2, and the retention of non-coordinating anions decreases. At higher pH values, processes 4 and 5 account for the presence of cation-exchange sites and the retention of non-coordinating cations (denoted  $\cdots \text{K}^+$ ). Between these two pH limits the anion- and cation-exchange capacity of the surface varies in accord with the solution pH. Retention data suggest that the conversion from an anion exchanger at low pH to a cation exchanger at high pH occurs somewhere between pH 6 and 7, a finding consistent with the reported isoelectric point for zirconia (see Table 8). Due to the presence of coordinating Lewis acid sites on zirconia's surface, ligand-exchange processes play a role in retaining some solutes, specifically those which act as hard Lewis bases, as depicted in reactions 6–10. Processes 6 and 7 describe the modification of the surface sites which occurs when a Lewis base is present in the eluent. Processes 8–10 show the exchange of an eluent Lewis base ( $\text{L}_1^-$ ) for a solute base ( $\text{L}_2^-$ ). The contribution of  $\text{H}_2\text{O}$  and  $\text{OH}^-$  to ligand exchange will depend strongly on pH. At lower pH values processes 7, 8, 9 and 10 are possible. At high pH values the contribution of processes 6 and 10 to the overall ligand-exchange process is likely to be minimal as the  $\text{OH}^-$  ion is a very strong, hard Lewis base. However, we would like to emphasize the importance of coordinatively bonded water in ligand exchange. *Ligand exchange does not proceed on silica which does not contain  $\sigma$ -coordinated water.*

### 3.5.4. Borate adsorption

The predictions of Stumm *et al.* [72] were confirmed in studies of the pH dependence of the adsorption of fluoride and borate on zirconia. Fig. 42 [16] shows the effect of pH on adsorption of  $F^-$  while Fig. 43 [199] illustrates the effect on the adsorption of boric acid.

Both figures also confirm the statements of Hingstone *et al.* [196] and Stumm *et al.* [72] that the maximum adsorption is likely to occur at a  $pH = pK_{a, HA}$ . Similar behavior was observed for the polymer–zirconia equilibria for polyacrylic acid adsorption [103]. Blackwell and Carr [177] have shown that the retention of benzoic acid derivatives at a given pH also depend on their  $pK_a$  values. Adsorption of boric acid on zirconia was characterized by electrokinetic measurements and potentiometric titration [199]. From the shifts in the  $pH_{pzc}$ , adsorption equilibrium constants have been derived using the site binding model [181]. Borate ion was assumed to form an ester bond with surface hydroxyl group. Calculated adsorption profile (amount adsorbed vs. pH) agrees well with earlier published maxima in the borate adsorption at  $pH \approx 9$  on

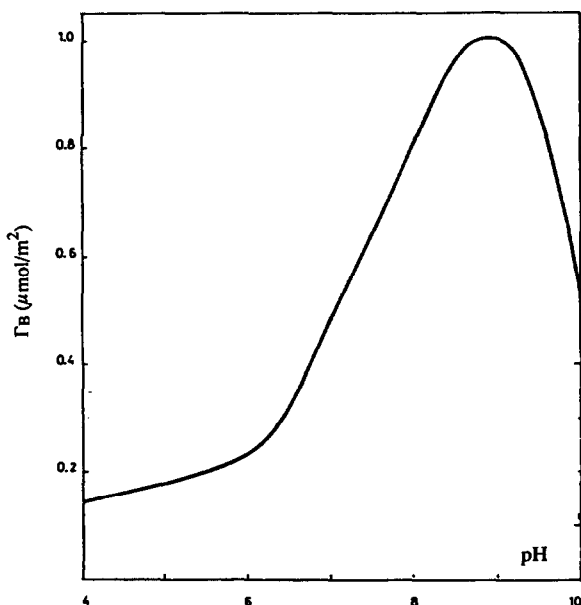


Fig. 43. Dependence of borate adsorption on pH ( $\Gamma_B$  = surface coverage in  $\mu\text{mol}/\text{m}^2$ ). From ref. 199.

alumina [200]. The maximum amount of borate adsorption should take place at pH 9 and the surface concentration was equal to *ca.*  $1 \mu\text{mol}/\text{m}^2$  for  $0.001 M H_3BO_3$  in  $0.1 M KNO_3$ . The affinity of zirconia for boric acid increases with an increase of pH (up to pH 9) but the affinity toward  $F^-$  decreases. Adsorption of boric acid from a  $1 M$  solution at pH 8.4 can decrease the  $F^-$  binding capacity from  $8.8 \mu\text{mol}/\text{m}^2$  to  $0.6 \mu\text{mol}/\text{m}^2$  [16], but at pH 6.1 boric acid has much lower affinity for the  $ZrO_2$  surface and in an elotropic series borate is seen to be weaker than fluoride, phosphate and even sulfate [177].

### 3.5.5. Complexes with fluoride

Zirconium forms a number of compounds with fluoride [87].  $ZrF_4$  exists as a stable, colorless, crystalline solid. The Zr atom is octacoordinated to fluorine and each fluorine atom is coordinated to two zirconium atoms.  $ZrF_4$  has a tendency to form fluorozirconates in solutions containing fluorides of uni- and divalent metals. Generally  $Zr-F$  in aqueous solution is more stable than coordinatively bonded water  $Zr \text{---} \text{OH}_2$  [87]. The displacement of  $H_2O$  coordinated to  $Zr^{4+}$  by  $F^-$  ion has been observed by Blackwell and Carr [16]. The fluorozirconates are decomposed by strong alkalis and their decomposition leads to hydrous zirconia [87].  $F^-$  ion adsorption on a zirconia surface is strongly dependent on pH which is shown in Fig. 42. A very similar curve for specific adsorption of  $F^-$  was also observed on  $\alpha\text{-FeOOH}$  [201]. Fluoride ion is the second strongest eluent (next to phosphate) in the elotropic series developed for zirconia at pH 6.1 [177]. Fluoride is a hard Lewis base and it is expected to interact strongly with Lewis acids. These strong interactions might be advantageous in liquid chromatography for the generation of a biocompatible zirconia stationary phase for the separation of proteins [17].

### 3.5.6. Complexes with phosphates

Zirconium phosphates ( $ZrP$ ) are well known materials with ion-exchange properties described in several books and reviews [34–36]. Zirconium phosphates have also been used in catalysis and

chromatography. Zirconium phosphates are solid acids—the distribution of acid sites and the catalytic activity of the phosphate in alcohol dehydrogenation reactions has been investigated [35]. Applications of ZrP in chromatography are not numerous; in gas chromatography amines were separated on columns packed with a gel in the  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  or  $\text{Mn}^{2+}$  forms using ammonia as the gas phase [202,203]. Gas–solid chromatography was used to measure the interactions of several aromatic and aliphatic adsorbates on  $\alpha$ -zirconium phosphate. Adsorption of hydrocarbons is said to occur at the surface and within cavities inside the structure. Oxygen-containing compounds interact strongly with the surface. This agrees with the catalytic properties of zirconium phosphate [204]. Zirconium phosphate was also tested as a gas chromatographic packing material for the separation of fatty acids [205]. Alkyl phosphate derivatives of  $\alpha$ -ZrP have also been used in HPLC [206]. Bis(octadecylphosphate) zirconium was used as a column packing for reversed-phase chromatography and the separation of several PAHs was achieved, but the mechanical strength of the packing was very poor [207].

Zirconium phosphate was impregnated in paper and used for chromatography. This modification was used for the separation of alkaloids [208].

Zirconium phosphate has a layered crystalline structure which is responsible for its intercalation ability. The intercalation mechanism of  $\alpha$ -ZrP was reviewed by Constantino [209].

$\alpha$ -Zirconium phosphate consists of zirconium layers capped on both sides by phosphate groups [36]. Granular zirconium oxide is appreciably broken down in concentrated phosphoric acid solution [26]. The strong tendency of phosphates to form layered structure is responsible for this. Schafer *et al.* [20] also noted that phosphate modification involves breaking of zirconium–oxygen bonds in the zirconia matrix.

The great affinity of zirconia for phosphate and the low solubility of zirconium phosphate in aqueous media [210] made the intentional modification of the surface of zirconia with phosphate an attractive concept. Phosphate-modified zirconia can be prepared in a straightforward fash-

ion by refluxing zirconia particles in dilute (0.1 M) phosphoric acid. A simplified scheme of the likely surface species on phosphate modified zirconia is given in Fig. 44.

The resulting phosphate-modified zirconia is a cation exchanger [36] and the acidity of the bonded phosphate increases substantially. The enhancement of the acidity of the surface complexes was also described by Stumm *et al.* [72]. Similar phenomena were observed for *o*-hydroxybenzoic acid adsorption on  $\text{Al}_2\text{O}_3$  [72,211], phosphoric acid adsorption on  $\alpha$ -FeOOH [72,201] as well as silicic acid adsorption on  $\alpha$ -FeOOH [72,201].

Under the “mildest” phosphating conditions, *i.e.* neutral pH, room temperature and short reaction times, phosphate physically adsorbs onto the surface of the particles (Fig. 44) especially onto the Lewis acid sites described earlier. At acidic pH and higher temperatures esterification of the phosphate with surface hydroxyls (Fig. 44) occurs. The purpose of such a modification would be to effectively block the strong

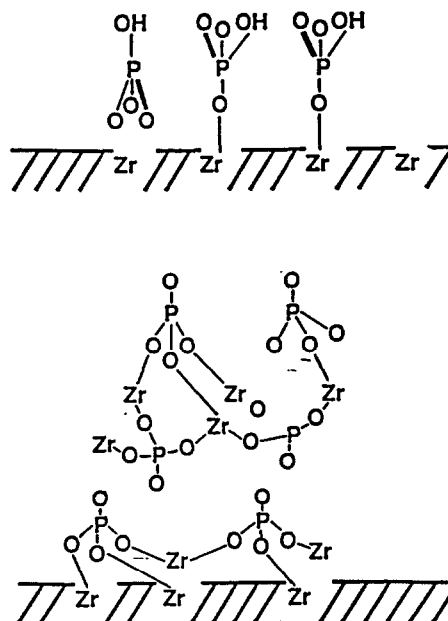


Fig. 44. Surface species on phosphate modified zirconia. Top, “mild” phosphating conditions; bottom, “rigorous” phosphating conditions. From ref. 20.

sites responsible for oxyanion interactions and thereby provide a more “bio-compatible” stationary phase. The widespread use of calcium phosphate (hydroxyapatite) in protein chromatography [212] and zirconium phosphate for transition metal ion separations [34–36] also suggested that a high-performance phosphate-modified zirconia support would be of interest as a chromatographic support.

### 3.6. Zirconia in liquid chromatography

Zirconia is an amphoteric material with anion-exchange properties in neutral and acid solutions, and cation-exchange properties in alkaline solutions [31–33].

The difference in the amphoteric acid–base chemistry of zirconia and titania surfaces relative to that of silica is clearly reflected in the chromatography of basic analytes. Strongly basic solutes are typically highly retained on silica and yield severely tailed peaks. By contrast, basic compounds with  $pK_b$  values as high as 11 have been separated on titania in normal-phase mode with high peak symmetry, as shown in Fig. 45 [24].

Before one starts experiments with zirconia columns, care should be taken to remove  $\text{CO}_2$  from the mobile phase. Carbon dioxide or carbonates will block Lewis acids sites by building up on the particle surface and gradually changing the overall character of the surface. Water used to prepare mobile phase should be boiled before use and use of a scrubber or pre-column is strongly advised [17,61].

Since the zirconia surface contains many adsorption sites and is able to ion and ligand exchange, it should, in most cases, be modified. We can take advantage of the chemical reactivity of the surface to “tailor” it according to our needs. Generally there are three classes of surface modification of zirconia: (1) dynamic, chemical modification—when a mobile phase containing a strongly interacting Lewis base is used; a large variety of such systems can be imagined, (2) permanent, chemical modification—*e.g.* silylation of the surface and (3) physical screening—*e.g.* coating the zirconia surface with a polymer or carbon layer.

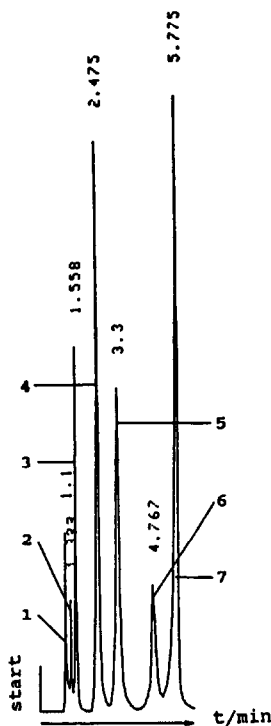


Fig. 45. Isocratic separation of basic analytes with calcined titania as a packing material;  $p_d = 5 \mu\text{m}$ ; injection volume,  $20 \mu\text{l}$ ; eluent, dichloromethane (relative water content 100%); flow rate 1 ml/min. Peaks: 1 = N,N-dimethylaniline, 2 = N-methylaniline, 3 = *o*-toluidine, 4 = aniline, 5 = *p*-toluidine, 6 = pyridine, 7 = diazepam. From ref. 24.

#### 3.6.1. Eluotropic series

Eluotropic series of solvents for such LC stationary phases as silica, alumina, *n*-alkyl bonded silica and carbon are well known [4,213,214]. It was of interest to develop a similar series for a zirconia surface. As shown in ref. 176, retention on  $\text{ZrO}_2$  surface is governed primarily by the Lewis basicity of the mobile phase and the basicity of the solute. It is thus obvious that an eluotropic series of Lewis bases should be possible. It must be kept in mind that the eluotropic series developed for one pH value may substantially change upon change in pH. The eluotropic series developed for benzoic acid derivatives at pH 6.1 as probes is shown in Table 11 [177]. The eluotropic series, as given in Table 11, is *roughly* in agreement with the sequence of

TABLE 11

## ELUOTROPIC SERIES BASED ON BENZOIC ACID DERIVATIVES ON ZIRCONIUM OXIDE [177]

The eluent was 20 mM of the Lewis bases shown below in 20 mM MES at pH 6.1. The flow rate was 1 ml/min at 35°C. Injections were 10  $\mu$ l volumes of 10 mM solutions in water. Detection was at 230, 254 and 280 nm. eno = Elution not observed, na = not assessed.

Eluent species	Capacity factor at pH 6.1			
	4-Nitro benzoate	4-Cyano benzoate	4-Formyl benzoate	4-Chloro benzoate
Phosphate	0.0	0.0	0.0	0.0
Fluoride	0.0	0.0	0.0	0.0
Ethylphosphonic acid	0.2	0.2	0.2	0.4
Malic acid	0.2	0.2	0.3	0.5
Citric acid	0.3	0.2	0.2	0.6
Ethylenediaminetetra- acetate	0.3	0.3	0.4	0.9
Oxalic acid	0.5	0.5	0.5	0.8
Aspartic acid	0.7	0.6	0.7	1.5
Succinic acid	0.6	0.7	0.8	1.4
Maleic acid	0.7	0.7	0.7	na
Glutaric acid	0.6	0.7	0.9	1.5
Adipic acid	0.7	0.7	0.9	1.7
Malonic acid	0.9	1.0	1.1	2.0
Pimelic acid	0.9	1.0	1.3	2.4
Sulfate	1.5	1.6	1.8	3.0
Glycolic acid	1.7	1.8	2.0	3.4
Boric acid	1.9	2.0	2.2	3.8
Nitrilotriacetic acid	2.1	1.6	2.2	5.2
Tartaric acid	2.9	1.4	2.2	5.8
Suberic acid	2.0	2.2	3.4	7.6
Thiosulfate	3.0	3.0	3.4	5.9
Iminodiacetic acid	3.1	3.1	3.9	7.7
Sebacic acid	3.8	3.0	3.0	20.6
Acetic acid	5.6	6.3	7.6	12.7
Tris(hydroxymethyl)- aminomethane	7.6	6.7	6.0	15.6
Formic acid	8.8	9.7	9.5	20.9
Sulfamic acid	10.8	11.1	15.3	23.5
Butyric acid	13.0	15.6	18.7	34.4
Urea	17.1	17.6	24.3	37.1
Bromide	17.0	18.2	22.9	40.4
Butanesulfonic acid	23.5	22.8	29.6	45.2
Guanidine hydrochloride	20.8	22.4	27.2	eno
Nitrate	24.7	26.0	33.5	57.6
Chloride	24.7	26.6	35.1	59.9
Thiocyanate	32.3	34.3	43.3	eno
Ethylene glycol	34.1	33.6	42.3	eno
Thiourea	41.7	43.9	eno	eno

binding strengths to zirconium. The strongest eluents can be classified as hard Lewis bases.

While the eluotropic strength is in good agreement with the expectations derived from hard-soft Lewis acid–base theory [215,216], it cannot be understood solely based on this theory. For example, although bromides are certainly softer Lewis bases than chlorides they exhibit stronger eluting properties than the latter [177].

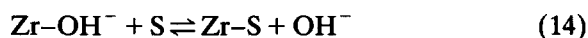
To understand the observed phenomena, the following model of retention was proposed: the zirconia surface is populated by ligands coordinated to a zirconium cation. In water these surface species are limited to bound hydroxyl, water and hydronium ion. At pH 6.1, for which an eluotropic series was developed, the concentration of surface hydronium ions can be neglected. In the mobile phase, molecules of eluent (E) and solute (S) will compete with water and hydroxide ion for the hard acid site ( $Zr^{4+}$ ). The total concentration of the surface species is:

$$C_{s,TOT} = [Zr-OH^-] + [Zr-S] + [Zr-E] + [Zr-H_2O] \quad (11)$$

where the terms in square brackets denote the concentrations of surface species. On the basis of the Regazzoni *et al.* [107,198] model of adsorption we can assume a competition between the eluent and the solute molecules:



The solute molecules can also compete with water and hydroxyl groups:



The concentration of the solute is negligible and therefore the term  $[Zr-S]$  in eqn. 11 can be neglected.

$$k' = \frac{\text{moles of solute on the surface}}{\text{moles of solute in the mobile phase}} \quad (15)$$

Thus:

$$k' = \frac{A[Zr-S]}{V_m[S]} \quad (16)$$

where  $A$  is the surface area of the support,  $V_m$  is

the volume of mobile phase in the column and  $[S]$  is the equilibrium mobile phase concentration of the solute.

Combining eqns. 11, 12 and 13:

$$k' = \frac{C_{s,TOT} K_s}{K_{OH}[OH^-] + K_E[E] + 1} \frac{A}{V_m} \quad (17)$$

where  $K_s$  = equilibrium constant for eqn. 13;  $K_E$  = equilibrium constant for eqn. 12;  $K_{OH}$  = equilibrium constant for eqn. 14.

Thus eqn. 17 should account for the variation of  $k'$  of a completely ionized Lewis base solute as the pH is varied and the variation in  $k'$  with a change in the concentration of a Lewis base eluting agent. All of this is based on the assumption of the homogeneity of the surface adsorption sites. It has been found [176] that the slope of a graph of  $k'$  vs. pH is close to  $-1$ . This can be interpreted to mean that the first term in the denominator of eqn. 8 is dominant. The dependence of  $\log k'$  of *p*-cyanobenzoic acid on the concentration of Lewis base ( $[E]$ ) in the mobile phase was found to decrease nearly monotonically as expected for a simple competitive displacement process. If eqn. 17 were rigorously valid then a plot of  $1/k'$  vs. the concentration of Lewis base in mobile phase would yield a straight line. As we can see in Fig. 46 this not the case.

A small number of strong adsorption sites could be responsible for the curvature of the lines. This is in agreement with numerous reports on the gas–solid interface where the  $Zr_{cus}^{4+}$  sites were found to be heterogeneous [64,98,153,157,158,164].

### 3.6.2. Chemical, dynamic modification

Despite the rather complex set of equilibria (eqns. 2–10) needed to describe zirconia's surface, we can take advantage of these for chromatography. Chromatography also appears to be a useful tool for investigating the surface chemistry of  $ZrO_2$ . Blackwell and Carr [176] examined the retention of a variety of benzoic acid derivatives with  $pK_a$  values ranging from 2.8 to 5.4 in the pH range 4.8–9.3. It should be noted that all of the acids were almost completely ionized over the entire range of pH values tested. Thus a pH dependence based on changes in the degree of

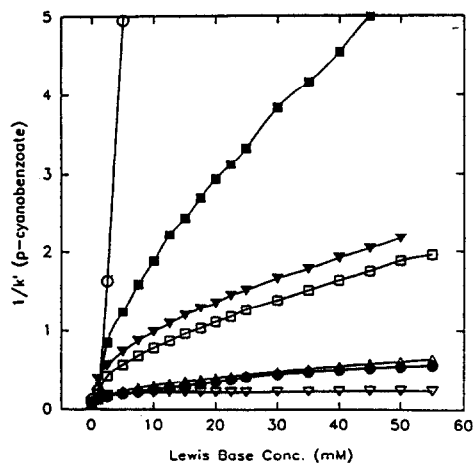


Fig. 46. (Capacity factor)<sup>-1</sup> vs. Lewis base concentration for *p*-cyanobenzoic acid. ○ = fluoride, ● = acetate, ▽ = butyrate, ▼ = succinate, □ = malonate, ■ = oxalate, ▲ = sulfate. The eluent was (500 - *X*) mM sodium chloride and *X* mM Lewis base in 20 mM MES at pH 6.1. The flow rate was 1.0 ml/min at 35°C and detection was at 254 nm. From ref. 177 (© American Chemical Society).

ionization of the solute would not be expected. In a parallel study Blackwell [217] examined the retention of benzoic acid derivatives on alumina.

Capacity factors were correlated with both the  $pK_a$  of the solute and the pH of the mobile phase. When the chromatographic capacity factor is "corrected" for its pH dependence its value on a zirconia surface can be predicted from the equation:

$$\log k' = 0.67pK_a - pH + C \quad (18)$$

where  $C$  = constant.

The above relationship (eqn. 18) for benzoic acid derivatives on zirconia is shown in Fig. 47 ([176]).

Similar behavior of benzoic acid derivatives has been found on alumina [217] and the relevant equation for their retention is:

$$\log k' = 0.33pK_a - pH + C \quad (19)$$

The weaker dependence on  $pK_a$  means that Al is not as strong a Lewis acid as Zr. The higher selectivity of zirconia over alumina toward benzoic acid derivatives has been noted. Retention of these compounds on alumina was said to be more complex than on zirconia and less dependent on the pH of the mobile phase since the

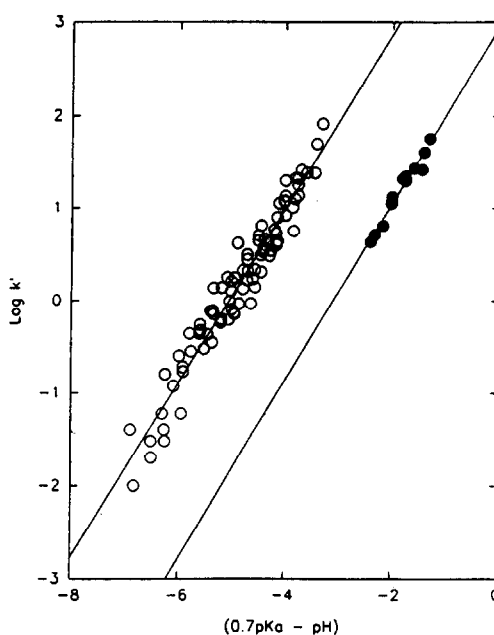


Fig. 47. Correlation of the capacity factors of *p*-benzoic acids with solute Brønsted acidity and solution pH. ○ = Aminosulfonate buffers, ● = acetate buffer. Regressions are least-squares fit. Reprinted from ref. 176.

slope of  $k'$  versus pH on alumina is lower than that on zirconia [176,217]. This means that retention on alumina cannot be fully predicted by eqn. 17.

Generally we can expect that other oxides ( $TiO_2$ ,  $Fe_2O_3$ ) will behave similarly toward polyoxo acids. Phosphonates, benzoic acids and acetic acid are known to adsorb on  $TiO_2$  surfaces [162].

The retention of benzoic acid derivatives is in accord with Pearson's theory [215,216] of hard and soft acids and bases and with Stumm *et al.*'s [72] postulate of ligand-exchange reactions at hydrous oxide surfaces. The results obtained on zirconia columns were compared to those on bonded phase strong anion exchangers which showed that in the range of pH values examined, no ion-exchange process was observed, and no correlation between retention and  $pK_a$  was found. Chromatographic selectivity toward the benzoic acids was much higher on zirconia surfaces than on the anion exchanger because their ionic properties do not differ significantly but their Lewis basicities differ greatly. The impor-



tance of complex formation on retention on zirconia is also reflected in zirconia's extreme sensitivity to isomerization. This has been demonstrated in the differences in retention of *ortho*-, *meta*- and *para*-hydroxy- and aminobenzoic acid isomers. The retention of the *ortho*-isomers is significantly enhanced as both functional groups can interact strongly with surface ligand-exchange sites. Isomeric selectivity was also much better for zirconia than for a conventional anion-exchange column which did not reveal any isomer selectivity. Kita *et al.* [76] could not confirm the existence of Lewis acid sites in the liquid–solid system by static methods. Lewis acidity of zirconia can, however, be confirmed by chromatography where ligand exchange at Lewis sites was observed [176,177].

In another paper, Blackwell and Carr [18] showed again that retention in aqueous media depends on the chemistry of the solute and eluent. This is shown in Table 12. Cationic solutes are not retained in chloride mobile

TABLE 12  
RETENTION AS A FUNCTION OF DISPLACING LEWIS BASE

Eluent contained 20 mM of displacing Lewis base with 20 mM MES at pH = 6.1. Flow rate was 0.5 ml/min at 35°C. Injections were 5  $\mu$ l of 10 mM solute in 20 mM sodium chloride 20 mM MES at pH = 6.1. Detection was at 230 and 254 nm using a diode array detector. n/a = Not available, eno = elution not observed.

Solute	Capacity factor		
	Buffer		
	Sodium chloride	Malic acid	Succinic acid
Guanidine	n/a	1.6	0.7
Imidazole	0.0	0.7	0.3
Benzylamine	0.0	0.8	0.4
Benzamide	0.0	0.0	0.0
Benzyl alcohol	0.0	0.0	0.0
Benzyl mercaptan	0.1	0.1	0.1
Phenylacetic acid	eno	0.0	0.2
Benzenesulfonic acid	0.9	0.1	-0.1
Phenol	0.2	0.0	0.0
Benzenephosphonic acid	eno	eno	eno

phases. In chloride media at pH 6.1 the surface hydroxyl groups are mostly in unionized state (see Fig. 41 and Table 10 for  $pK_{a1}^{int}$  and  $pK_{a2}^{int}$  data) and the ionic strength of the eluent is high enough to displace any solute bonded by an ion exchange. When stronger Lewis bases are present (such as dicarboxylic acids) in the mobile phase, they generate a negative charge on the zirconia surface thereby causing adsorption of cations and the retention of cationic solutes change significantly. Table 12 also shows that non-electrolytes are non-retained in all buffers. This means that cationic compounds are not retained by hydrogen bonding and/or Van der Waals forces. In contrast anionic solutes were retained in chloride mobile phase but they are weakly retained when a Lewis base eluent is present in the mobile phase. This confirms again that the dominant retention process is ligand exchange [18].

The most interesting application of zirconia in chromatography is the separation of proteins. Zirconia as a base-stable stationary phase not only allows separation of those molecules at high pH values but also provides an easily "cleaned" surface. This stability offers many obvious chromatographic advantages. It is also significant in terms of the use of zirconia for the downstream processing of proteins because the use of hot alkaline media is a routine sanitization procedure in these applications.

Depyrogenation [218–220] especially requires vigorous conditions, for instance, 0.1 M sodium hydroxide in 95% aqueous ethanol or 80% aqueous dimethyl sulfoxide. In this sort of aggressive environment zirconia offers a distinct advantage since silica-based materials are destroyed under these conditions and polymer-based materials are limited by their hydrolytic, thermal and mechanical stability. Thus there is considerable interest in the development of a zirconia-based support for protein separations, hopefully without the irreversible adsorption problems common to silica-based supports and the unacceptable physical and mechanical properties of hydroxyapatite gel-type and polymer-type supports.

Initial attempts to elute proteins from bare zirconia were unsuccessful because it has a high

affinity for some functional groups, such as carboxylic acids. However, zirconia does not show the same affinity for amines that leads to irreversible protein adsorption on silica-based supports. Protein separations are possible by recognizing and taking advantage of some of the very same surface chemistry. Blackwell and Carr [221] have shown that a variety of proteins can be chromatographically separated on zirconium oxide particles. To elute the proteins, a mobile phase must contain an appropriate concentration of a hard Lewis base. The initial concentration of the base appears to be a critical parameter in achieving acceptable retention and peak shape. In practice the eluent should contain phosphate, fluoride, polyvalent carboxylates or organophosphate ligands. In a subsequent paper Blackwell and Carr [222] demonstrated an application of the ion-exchange properties of zirconia for protein separations. The zirconia surface can be loaded with  $\text{Cu}^{2+}$  ions ( $3.9 \mu\text{mol}/\text{m}^2$ ). Providing  $\text{Cu}^{2+}$  ions remain in the mobile phase, it is possible to apply this type of copper-loaded zirconia to the separation of proteins. The solutes were said to interact with the stationary phase by a ligand-exchange mechanism.

Another example of the chemical flexibility of the zirconia surface is an application of a borate-modified zirconia surface [221] to the separation of proteins. The chromatographic behavior of this type of stationary phase correlated well with the properties of a borate-modified surface as derived from data obtained by static liquid–solid interface studies [199].

A more “universal” protein support can be produced by taking advantage of the very strong interaction of fluoride with zirconia. A protein separation on unmodified zirconia using a sodium sulfate gradient in 20 mM sodium fluoride is shown in Fig. 48.

There is no relationship between protein capacity factors and their isoelectric points. This is shown in Fig. 49.

Both cationic and anionic proteins are retained on zirconia in fluoride media, analogous to calcium hydroxyapatite and in contrast to the retention behavior reported for zirconium phosphate. The data in Table 13 show that the retention of proteins decreases significantly with

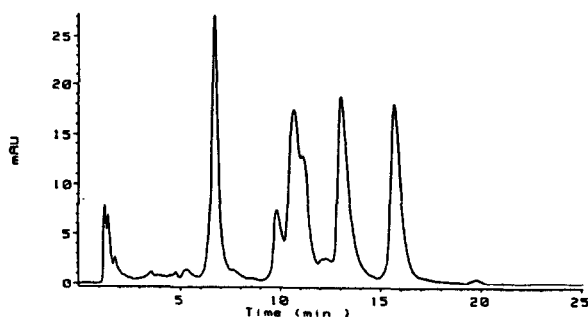


Fig. 48. Protein separation on fluoride modified zirconium dioxide. A linear gradient of 0 to 0.75 M  $\text{Na}_2\text{SO}_4$  in 100 mM NaF and 20 mM MES at pH 5.5 was used. Flow rate was 0.5 ml/min at 35°C. Protein loading: 4.4  $\mu\text{g}$  lysozyme, 15.4  $\mu\text{g}$   $\alpha$ -chymotrypsin, 13.6  $\mu\text{g}$  myoglobin, 15.4  $\mu\text{g}$  cytochrome *c*. From ref. 17.

increasing sodium fluoride concentration in the mobile phase, suggesting that the Lewis acid–base interactions with the surface zirconium(IV) sites play an important role in retention.

The use of bare zirconia for protein separations with fluoride-containing mobile phases has the additional advantage of high loading capacity, nearly quantitative mass and activity recoveries and the aforementioned stability of unmodified zirconia.

Zirconia is well known to strongly interact

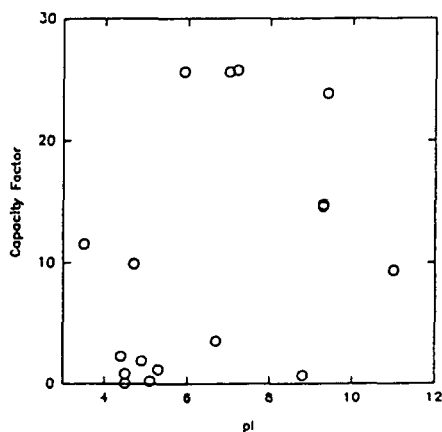


Fig. 49. Correlation of capacity factor with *pI*. Gradient elution from 0 to 0.5 M  $\text{Na}_2\text{SO}_4$  in 30 min. Both buffers contained 20 mM NaF and 20 mM MES at pH 6.2 at 35°C. Flow rate was 0.5 ml/min and detection was at 280 nm. From ref. 17.

TABLE 13

## PROTEIN RETENTION IN FLUORIDE MEDIA [61]

Buffers consisted of (A) sodium fluoride 20 mM MES pH = 5.5 and (B) buffer A with 0.5 M sodium sulfate added. Gradient was 0 to 100% B in 30 min then back to 0%B in 15 min with a 15-min equilibration period. Flow rate was 1 ml/min at 35°C with detection at 280 and 410 nm. Typical injections were 10 µg protein in 20 mM MES at pH = 5.5. eno = Elution not observed.

Protein	<i>pI</i>	Capacity factor		
		0.50 M NaF	0.10 M NaF	0.02 M NaF
Ovalbumin	4.7	10.6	17.3	eno
Bovine albumin	4.7, 4.9	14.2	23.1	32.5
Human albumin	4.6–5.3	17.0	25.3	34.1
Transferrin, apo	5.9	16.6	26.5	31.2
Myoglobin	6.8, 7.3	3.5	16.7	24.6
Hemoglobin	6.9–7.4	3.9	15.7	24.2
Alc. dehydrogenase	8.7–9.3	21.2	eno	eno
α-Chromotrypsin	8.8	2.3	13.2	18.1
Ribonuclease A	9.3	3.3	15.9	19.7
Ribonuclease B	9.3	3.6	6.8	11.1
Cytochrome c	9.4, 9.0	5.1	22.6	28.4
Lysozyme	11.0	0.2	5.2	10.3

with phosphoric acid. A phosphate-modified surface can also be utilized for the chromatography of proteins. Since phosphate-modified zirconia is a cation exchanger it can also be used for chromatography in various cationic forms: Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup> [21] or Cu<sup>2+</sup> [223]. <sup>31</sup>P magic angle spinning NMR spectra [20] show the presence of covalently bonded phosphate and phosphate adsorbed on the surface. It was also proved that to bond the phosphate covalently more rigorous conditions such as lower pH, higher temperature and longer exposure time are required. The phosphated support behaves as a classical cation exchanger. It does not behave as a mixed-mode system analogous to hydroxyapatite, wherein interactions with phosphate and calcium are both involved in protein retention [212]. It is likely that phosphate ions adsorb onto and interact so strongly with surface zirconium sites that only the phosphate sites are “available” for interaction with proteins. This would explain the cation exchange behavior of ZrP rather than a hydroxyapatite-like behavior. Proteins are retained mainly by an ion-exchange process; at pH > 6 proteins with low *pI* are not retained while proteins with high *pI* are retained.

Retention also decreases when the competing ion concentration is increased. That retention is due to cation exchange is also supported by the fact that the type of displacing cation has a significant effect on retention [21]. Phosphate-modified zirconia appeared to be very stable column packing, but it requires the presence of phosphate in the mobile phase. This is shown in Fig. 50.

Table 14 summarizes the retention of proteins on various chemically modified surfaces of zirconia. The table shows the chemical “tunability” of the surface. Taking advantage of the rather complex surface equilibria, it is possible to “adjust” the surface properties to the particular needs of the separation.

It should be emphasized here that Table 14 is not a comprehensive list of all possible surface modifications. For example, proteins can be also chromatographed on metal-substituted phosphate-modified zirconia [21,223]. Recovery of proteins is an important characteristic, particularly for preparative separations. Table 15 demonstrates that quantitative recovery can be obtained on both phosphate- and fluoride-modified zirconia columns.

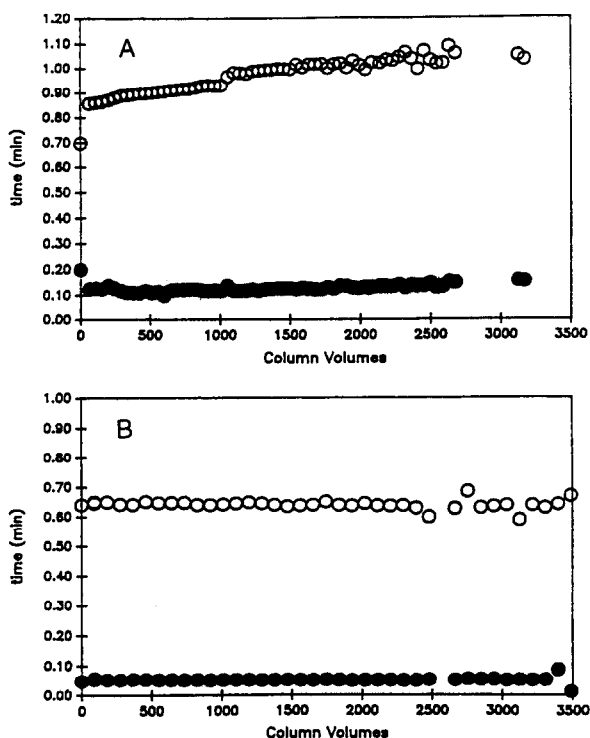


Fig. 50. Stability of phosphate-modified zirconia using benzoic acid as a probe solute. Column: 10–15  $\mu\text{m}$ , 100 Å ZrP (0.1),  $5 \times 0.46$  cm. Mobile phase: (A) 1 mM pH 7.0, MOPS buffer, 0.5 ml/min; (B) 20 mM pH 7.0,  $\text{K}_2\text{HPO}_4$  buffer, 0.5 ml/min, detection at 254 nm. From ref. 21.  $\circ$  = retention time,  $\bullet$  = peak width.

### 3.6.3. Chemical, permanent modification

While the understanding of zirconia surface chemistry from the chromatographic studies described above is invaluable, it is a fact of chromatographic life that most separations are not done on highly active unmodified supports. It is reasonable to expect that the successful application of zirconia supports to a variety of chromatographic separations will require access to facile and controllable surface modification schemes. The highly developed siloxane chemistry used to tailor the surface properties of silica supports would seem a logical place to begin. The widespread use and popularity of silica-based reversed phases draw attention to the possibility of obtaining reversed phases based on zirconia. Since zirconia contains many surface hydroxyl groups, the use of silane reagents is

very seductive. In fact there are a few reports in the literature concerning silanization of zirconia surfaces. Rigney [243] attempted to modify the surface with mono- and tri-functional silanes. Attempts to prepare *stable* coatings with octyldimethylchlorosilane and alkoxy silanes were unsuccessful. Although coverage up to several  $\mu\text{mol}/\text{m}^2$  could be obtained the resulting phases were evidently not usefully stable under HPLC conditions. The phases were particularly unstable during extraction with methanol [243]. Modification with trifunctional octyltrichlorosilane led to a stable stationary phase with a coverage of *ca.* 3.3  $\mu\text{mol}/\text{m}^2$ . Trüdinger *et al.* [24] have reported on a successful silanization of the zirconia surface with a trifunctional silane (*n*-octadecyltrimethoxysilane). The resulting phase was said to be extremely stable—withstanding 500 h at pH 12. Separation of polycyclic aromatic hydrocarbons on the phase has been reported. Yu and El Rassi [126] silanized non-porous zirconia particles with mono- and trichlorooctadecylsilanes. Monomeric octadecyl phase was very unstable in pH 2 as well as pH 12. An essentially polymeric octadecyl phase was also unstable although its properties seem to stabilize after 1000–2000 column void volumes of mobile phase. Due to extremely low surface area no coverage values are provided. Several applications of the polymeric octadecyl zirconia are provided by the authors [126]: separation of PAHs, *p*-nitrophenylmaltooligosaccharides, dansylated amino acids, peptides and proteins. Amati and Kováts [84] silanized a zirconia surface with trimethylsilyldimethylamine (TMS-A) and 3,3-dimethylbutyl–dimethylsilyldimethylamine (DMB-A) and with the corresponding silanols (TMS-O) and (DMB-O). They have obtained 3.45  $\mu\text{mol}$  TMS/ $\text{m}^2$  and 4.6  $\mu\text{mol}$  TMS/ $\text{m}^2$  with amine and silanol, respectively, as well as 2.45  $\mu\text{mol}$  DMB/ $\text{m}^2$  and 3.5  $\mu\text{mol}$  DMB/ $\text{m}^2$  with amine and silanol, respectively. However, these surfaces were not tested under chromatographic conditions. Reaction time was very long (170 h), according to the procedure developed earlier by the same group [226]. It is important to recognize that the replacement of a silicon atom in a siloxane bond by a heteroatom generally produces M–O–Si bonds which are far

TABLE 14

## PROTEIN RETENTION WITH IONIC STRENGTH GRADIENTS AND CONSTANT LEWIS BASE CONCENTRATIONS [221]

Linear gradient elution from 2% B to 100% B in 15 min with a 15-min equilibration period. Flow rate was 0.5 ml/min at 35°C. Injections were 10- $\mu$ l volumes of 10 mg/ml solutions of protein in 20 mM TABS at pH 8.4. Detection was at 280 and 410 nm. Buffer A: 20 mM Lewis base in 20 mM TABS at pH 8.4; buffer B: buffer A with 1 M sodium chloride. Lewis bases: A = sodium phosphate, B = sodium fluoride, C = boric acid, D = citric acid, E = aspartic acid, F = tartaric acid, G = imidodiacetic acid, H = aminomethylphosphonic acid, I = ethylphosphonic acid, J = O-phospho-DL-serine. PEP = Pepsin, GLOX = glucose oxidase, TINH = trypsin inhibitor, OVA = ovalbumin, HSA = human serum albumin, HEXO = hexokinase,  $\beta$ LAC =  $\beta$ -lactoglobulin, LIP = lipase, ATRH = apotransferrin, MYO = myoglobin, HEMO = hemoglobin,  $\alpha$ CHY =  $\alpha$ -chymotrypsin, CYTC = cytochrome c, RNA = ribonuclease A, RNB = ribonuclease B, LYS = lysozyme. eno = Elution not observed.

Protein	Capacity factors										
	A	B	C	D	E	F	G	H	I	J	
PEP	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3
GLOX	-0.3	-	-0.3	-0.3	1.2	-0.3	-	-0.3	-0.3	-0.3	-0.3
TINH	-0.2	0.1	0.1	0.0	0.2	0.0	0.2	0.0	-0.2	-0.2	-0.2
OVA	-0.2	-	-	-0.2	-	0.2	-	-0.2	-0.2	-0.2	-0.2
HSA	-0.3	-	-0.3	-0.3	-0.3	-0.3	-	-0.3	-0.3	-0.3	-0.3
HEXO	-0.2	1.6	1.9	0.5	1.3	1.3	3.0	0.1	-0.3	-0.3	0.1
$\beta$ LAC	-	-	-	-	-	-	-	-0.3	-0.3	-0.3	-0.2
LIP	0.2	1.2	1.3	0.5	1.3	1.3	2.2	0.1	0.5	0.5	0.1
ATRH	12.0	-	-	0.1	-	0.0	-	-0.1	-0.2	-0.2	-0.2
MYO	11.6	14.5	13.4	1.1	26.9	3.8	-	0.3	0.7	0.1	0.1
HEMO	19.4	20.0	14.4	-0.1	-	-0.1	-	-0.1	-0.2	-0.1	-0.1
$\alpha$ CHY	13.8	-	-	12.5	22.5	14.5	-	6.3	14.2	8.8	8.8
CYTC	23.4	-	-	23.3	-	26.2	-	11.3	26.4	16.5	16.5
RNA	15.1	13.0	13.2	9.9	14.1	11.0	18.8	6.6	11.3	7.4	7.4
RNB	11.1	12.8	13.0	8.5	13.7	9.7	18.9	3.8	9.5	6.2	6.2
LYS	10.9	9.4	11.2	10.5	12.8	10.2	12.6	5.9	15.1	8.1	8.1

TABLE 15

## RECOVERY OF PROTEINS FROM ZIRCONIA COLUMNS

Protein	Phosphate-modified ZrO <sub>2</sub> [21]	Fluoride-modified ZrO <sub>2</sub> [17]	
	Enhanced assay <sup>a</sup>	Enhanced assay	Micro assay <sup>a</sup>
Ribonuclease A	95% ( $\pm$ 5%)	-	-
Cytochrome c	87% ( $\pm$ 7%)	-	-
Lysozyme	95% ( $\pm$ 5%)	103.9 $\pm$ 2.5%	101.2 $\pm$ 2.2%
Myoglobin	-	107.7 $\pm$ 6.1%	95.7 $\pm$ 4.1%

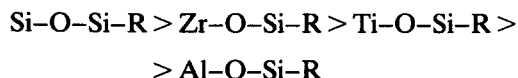
<sup>a</sup> See refs. 224 and 225.

less stable than the Si–O–Si bond [227], and therefore the stability of silanized metal oxides will not equal that of silanized silica [228,229].

Rigney [243] discussed the instability of the

Si–O and Zr–O bonds in terms of their ionic character. A siloxane bond is determined to be 50% ionic while a Zr–O bond is 67% ionic. This is in agreement with the order of hydrolytic

stability of silanized oxides established by Schindler and Schmidbaur [229]:



Thus Zr–O–Si bonds should be more susceptible to hydrolysis than Si–O–Si. However, Trüdinger *et al.* [24] observed the stability of their reversed phase at pH 12 for 500 h. Since the motivation for evaluating alternatives to silica arises at least in part from the inherent instability of siloxane-bonded supports, the lower stability of silanized zirconia is of concern, and has led to a focus on modification schemes other than silanization.

Other attempts to produce reversed phase on zirconia-based surface were also only partly successful [243]. In contrast to silica, Zr–C single bonds are very uncommon and we can hardly expect a successful modification of the type Zr–O–Zr–C. Another attempt to prepare a reversed phase was also undertaken by Rigney [243] who modified the surface by adsorption of organophosphates. Octylphosphonic acid adsorbed (at a surface concentration of  $2.6 \mu\text{mol}/\text{m}^2$ ) on the surface did indeed exhibit reversed-phase behavior. However, the phase was not stable in alkali. Another approach to get a non-polar surface on zirconia particles was presented by Ghaemi and Wall [106]. The surface was dynamically modified with a hydrophobic quaternary amine.

### 3.6.4. Physically screened zirconia particles

**3.6.4.1. Polybutadiene-coated zirconia.** Chemically stable modification of the chromatographic performance of zirconia was accomplished by deposition and cross-linking of polybutadiene (PBD) [25] in the manner reported by Schomburg and co-workers for the modification of silica and alumina [230,231]. The result is a remarkably stable reversed-phase support. After a slight initial decrease in retention, the retention of a non-polar probe solute showed no further decrease in  $k'$  when over 30 000 column volumes of methanol–0.1 *M* sodium hydroxide (50:50) were passed throughout the column [25]. Analysis of the column effluent for zirconium by ICP-AES showed no measurable level of zirconium. It should be noted that under these same conditions, a commercial polybutadiene-modified alumina column failed due to bed collapse after 8000 column volumes. In addition to this chromatographic stability test, the stability of polybutadiene-modified zirconia and alumina was evaluated by exposing columns packed with these supports to a mobile phase of 1 *M* sodium hydroxide at 100°C. The results of ICP-AES analysis of the column effluents are given in Table 16.

No zirconium was found in the column effluent. In contrast, it is obvious from the data in Table 16 that alumina dissolves to a significant extent during the first hour of exposure to these conditions. In fact, after 3.25 h of exposure the amount of aluminum dissolved corresponded to

TABLE 16

EXPOSURE OF POLYBUTADIENE-COATED SUPPORTS TO "STERILIZING" CONDITIONS [25]

Column	Time (h) <sup>a</sup>	Al [ $\mu\text{g}/\text{ml}$ ] <sup>b</sup>	Si [ $\mu\text{g}/\text{ml}$ ] <sup>b</sup>	Zr [ $\mu\text{g}/\text{ml}$ ] <sup>b</sup>
Al <sub>2</sub> O <sub>3</sub> –PBD	1	680	13.6	– <sup>c</sup>
Al <sub>2</sub> O <sub>3</sub> –PBD	3.25	243	3.3	– <sup>c</sup>
Zirconia–PBD	1	– <sup>c</sup>	1.6	– <sup>c</sup>
Zirconia–PBD	3.25	– <sup>c</sup>	2.1	– <sup>c</sup>
Zirconia, unmodified	1	– <sup>c</sup>	2.4	– <sup>c</sup>
Blank (1 <i>M</i> NaOH)		– <sup>c</sup>	1.5	– <sup>c</sup>

<sup>a</sup> Time of exposure to 1 *M* NaOH at a flow rate of 1 ml/min; T = 100°C.

<sup>b</sup>  $\mu\text{g}/\text{ml}$  in column effluent as determined by ICP-AES.

<sup>c</sup> Less than the detection limit (0.04  $\mu\text{g}/\text{ml}$ ) by ICP-AES.

more than 10% of the alumina originally present in the column. Retention data for a variety of uncharged non-polar solutes on this type of reversed-phase support were comparable to data on a conventional silica bonded phase reversed-phase support. However, there was evidence of strong, irreversible interactions between certain solutes and the zirconia support. In fact these interactions were expected based on considerations of zirconia's unique surface chemistry. For example, carboxylic acids and organophosphate solutes irreversibly adsorbed. These interactions are analogous to the well known interactions of amines with an acidic silica surface. Such interactions lead to problems with peak tailing, poor efficiency, low recoveries and hysteresis effects.

These data lead us to believe that some of the surface sites are still available for interactions. By taking advantage of the strong interaction of phosphates with zirconia, the number of sites could be measured in static adsorption experiments. Even the thickest layers of PBD allowed about  $2.3 \mu\text{mol}/\text{m}^2$  of phosphate to bind to zirconia. Also chromatographic results confirm that a part of  $\text{ZrO}_2$ -PBD surface is not covered by the polymer. This leads to a mixed-mode retention mechanism.

One possible strategy for inhibiting interactions with zirconia's surface is the use of phosphate-containing mobile phases. Table 17 dem-

onstrates the effect of various levels of inorganic phosphate on the chromatographic data of several test solutes. If these solutes were retained solely by a reversed-mode mechanism, benzoic and toluic acids should elute before benzene and toluene respectively. In 1 mM phosphate benzoic acid is slightly more retained than benzene. In 10 mM and 100 mM phosphate both acids elute before the related hydrocarbons. This indicates that chromatography on  $\text{ZrO}_2$ -PBD can be improved by the addition of phosphate to the mobile phase [243]. This is in contrast with the observed "substantial deactivation" of silicas coated with PBD [232]. PBD-coated zirconia was also used for several separations by Hanggi and Marks [244].

**3.6.4.2. Polystyrene-coated zirconia.** Particles of zirconia coated with polystyrene were used to separate several mixtures of basic compounds with mobile phases containing  $\text{HNO}_3$  or  $\text{NaOH}$ . The separation of acidic compounds showed lower efficiency even in the presence of an acidic mobile phase [81].

**3.6.4.3. Carbon-coated zirconia.** Carbon-based HPLC supports have been the subject of intensive studying for the last few years [213,233–235]. Carbon packings differ substantially from other reversed-phase supports. They are commonly more retentive toward polar compounds and are often more selective for the separation

TABLE 17

EFFECT OF PHOSPHATE CONCENTRATION ON RETENTION ON  $\text{ZrO}_2$ -PBD

Column, 5 cm  $\times$  0.46 cm I.D., packed with 10–15  $\mu\text{m}$   $\text{ZrO}_2$ -PBD. Flow rate, 1 ml/min at 40°C. Injection volume 5  $\mu\text{l}$ ; solute concentration, 1 mM. eno = No elution observed at  $k' < 100$ .

Solute	$k'$		
	1 mM $\text{H}_3\text{PO}_4$ <sup>a</sup>	10 mM $\text{H}_3\text{PO}_4$ <sup>b</sup>	100 mM $\text{H}_3\text{PO}_4$ <sup>c</sup>
Benzene	0.58	0.60	0.47
Benzoic acid	0.64	0.53	0.24
Toluene	1.0	1.1	0.84
Toluic acid	0.90	0.72	0.40
Benzylamine	0.32	0.36	0.23
Phenylphosphonic acid	eno	eno	0.13

<sup>a</sup> Mobile phase MeOH–1 mM  $\text{H}_3\text{PO}_4$  (50:50, v/v) adjusted to pH = 3.

<sup>b</sup> Mobile phase MeOH–10 mM  $\text{H}_3\text{PO}_4$  (50:50, v/v) adjusted to pH = 3.

<sup>c</sup> Mobile phase MeOH–100 mM  $\text{H}_3\text{PO}_4$  (50:50, v/v) adjusted to pH = 3.

of isomers and homologues. They also have a much greater chemical stability over a wider pH and temperature range than bonded phases. The drawbacks of carbon packings are often one or more of the following: poor mechanical stability, low surface area, a heterogeneous surface (and therefore low loading capacity) and non-uniform pore structure. Zirconia particles coated with a carbon layer developed by Funkenbush *et al.* [116] seem to be substantially different from other carbon supports. The process of carbon coating is carried out by passing organic vapors over the zirconia particles at an elevated temperature and reduced pressure. The most common conditions are: 700°C and 5–10 Torr (1 Torr = 133.322 Pa). This procedure creates a uniform carbon coating on the porous particles. It is possible to cover more than 97% of the available zirconia surface [23,116,236].

For this purpose zirconia has important advantages over silica and alumina. It can be heated to high temperatures (*i.e.* >500°C) with little change in pore structure. A variety of organic compounds have been used as the source of carbon: toluene, cyclopentane, heptane, iso-octane, 1,7-octadiene and *n*-butanol. It has been found that the precursor used for the cladding has a major effect on the nature of the final support. The loading capacities of the final phases derived from saturated hydrocarbons and 1-butanol were satisfactory. Phases derived from toluene and 1,7-octadiene indicated a very strong dependence of capacity factors on the amount of polar solute injected [22,236]. Similarly, efficiencies and mass transfer characteristics of the first group of columns were better than for those packings derived from unsaturated hydrocarbons. A small number of strongly interacting adsorption sites were blamed for the behavior of carbon deposited from unsaturated hydrocarbons [236]. This situation resembles the problems observed with silica wherein a small population of strongly interacting sites causes considerable difficulties [83,97]. On carbon these sites are the cause of low linear capacity and poor efficiency for certain solutes (*e.g.*, nitroaromatics, phenols, ketones, aldehydes). This situation can be addressed to a certain extent by hydrogenation [23,236] of the surface at elevated temperatures

to remove high-energy adsorption sites and/or by modifying the support by deposition and cross-linking of polybutadiene.

The resulting chemical-vapor deposited (CVD) carbon-coated material is useful as a reversed-phase support for liquid chromatography. As expected, this material demonstrates much greater selectivity for the separation of both non-polar and polar isomers than do conventional reversed phase support. This is shown in Fig. 51.

The isomers of butylbenzene are more completely resolved in less time on a carbon-clad zirconia column compared to a Hypersil ODS column, despite the greater efficiency of the Hypersil column ( $N_{\text{ODS}}(\text{butylbenzene}) = 2650$ ;  $N_{\text{zirconia}}(\text{butylbenzene}) = 1665$ ).

The separation of isomers on the carbon-zirconia column is trivial. The separation illustrated in Fig. 51 was carried out on only 16 m<sup>2</sup> of packing material in the column. The column can also easily separate *cis*- and *trans*-isomers. The separation of *cis*- and *trans*-stilbenes was achieved on a different carbon column by Belliardo *et al.* [237] where the available surface area exceeded 1300 m<sup>2</sup>. Carbon-clad zirconia supports are stable at elevated temperature and pH. This is comparable to that of unmodified zirconia and polybutadiene-coated zirconia.

**3.6.4.4. Polymer-coated carbon-clad zirconia.** When the carbon-clad zirconia is covered by a polymer, some of the unique properties of the carbon-clad material are lost. This is due to the mechanism of retention changing from an “adsorption-like” process on the carbon surface to a more “partition-like” process in the polymer film. The resulting phase can be considered as a composite material with high chemical and mechanical stability. Polymer coating greatly alters the characteristics of carbon-clad zirconia. The solute–adsorbent interactions are significantly weakened [22,238]. However, polymer coating improves the efficiency of the packing and the mass transfer characteristics. The chemical stability has proven to be remarkable. It withstands *ca.* 2000 column volumes of methanol–water (50:50) pH 12 mobile phase at 80°C with no measurable loss of carbon [22,238]. Generally polybutadiene coating improves the performance



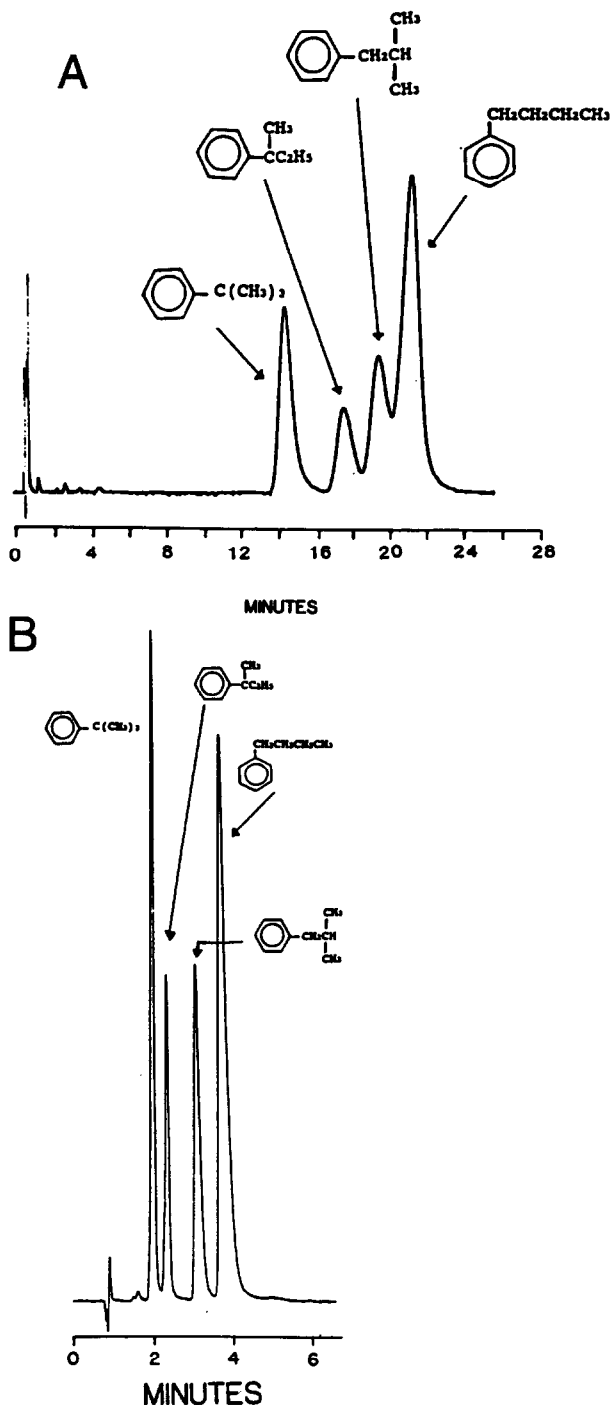


Fig. 51. Separation of butylbenzene isomers: (A) Hypersil ODS column,  $10 \times 0.21$  cm,  $5 \mu\text{m}$  particles,  $0.5$  ml/min, water-ACN (60:40, v/v),  $254$  nm detection. (B) CVD carbon-clad zirconia column,  $10 \times 0.21$  cm,  $8 \mu\text{m}$  particles,  $0.4$  ml/min, water-ACN (40:60, v/v),  $254$  nm detection. From ref. 23 (© American Chemical Society).

of the carbon-clad zirconia columns, decreases retentivity and increases loading capacity. However, some selectivity is lost [22].

### 3.6.5. Other zirconia applications in chromatography

Spherical particles of zirconia have also been used as the stationary phase for thin-layer chromatography [239] with diffuse reflectance Fourier transform infrared detection. Detection on zirconia was said to be better than on silica and alumina.

It is also worth mentioning applications of  $\text{Zr}(\text{OH})_4$  in paper chromatography where it has been used for the separation of amino acids [240,241].

## 4. CONCLUSIONS

Zirconia is a material which has many unique properties which make it attractive as a chromatographic support, notably, its excellent chemical stability and unique surface chemistry. Preparation of stable, mechanically strong particles of the desired particle and pore diameters for HPLC purposes can be provided by two modern techniques; oil emulsion and coacervation. Zirconia is expected to have lower specific surface area and pore volume compared to silica. However, due to its higher density, the surface area available in a chromatographic column and the porosity should be comparable to that of silica.

Despite many efforts to understand the surface properties of zirconia there still remains a great deal to be done so as to fully understand its complex properties. The main difficulty in achieving a wider variety of applications of zirconia in HPLC is probably a lack of knowledge and poor understanding of zirconia's surface chemistry. The main purpose of this review has been to gather as much data as possible and to shed some light on zirconia's surface chemistry. The properties of zirconia are very dependent on its synthesis. Moreover zirconia's properties are shown to change over long periods of time. To overcome all these difficulties it is decidedly better to use crystalline zirconia *i.e.* monoclinic rather than amorphous zirconia. To

assure the reproducible properties of the chromatographic zirconia a hydroxylation of the surface by washing with base and acid is recommended. Zirconia is catalytically active but this seems to be limited to cases where the surface is completely dehydroxylated. It seems that the activity can be suppressed under HPLC conditions.

Due to its unique surface chemistry zirconia offers many possibilities for use in chromatography; it can be used as a bare support, it can be dynamically modified, it may be coated with polymers or with inorganic overlayers. Stable reversed phases can be prepared by polymer deposition and cross-linking or chemical vapor deposition. Lewis acid–base interactions play an important role and can be troublesome with respect to the chromatography of some solutes, particularly oxyanions. These same interactions can be exploited to allow protein separations on the bare support. The usefulness of zirconia for protein separations and its stability under the aggressive conditions required for sanitation suggest many applications in the chromatography and purification of biomolecules. Much work remains to be done to develop a complete understanding of the complex acid–base chemistry of these supports and in producing modified surfaces for other applications. So far, no stable, monomeric, chemically bonded phase on zirconia surface has been reported and this seems to be the most serious disadvantage in comparison to silica-based HPLC packings.

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