

## Preparation and characterization of mesoporous zirconium oxide. Part 2.

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### Abstract

Mesoporous zirconium oxides were prepared by the sol–gel procedure under basic catalysis and in the presence of a series of surfactants:  $C_nH_{2n+1}N(CH_3)_3Br$ , with  $n = 8–18$ . Zirconium propoxide was used as a precursor. Basic conditions were created by NaOH (pH > 11) or ammonia (pH = 10). The influence of the preparation parameters was examined by modifying several parameters such as Zr:H<sub>2</sub>O and Zr:surfactant molar ratios. The sol-step and then the polymerization step were achieved at different temperatures. Drying of the samples was carried out by lyophilization, or in vacuum oven at 383 K for 48 h. Calcination of the materials was made on the basis of TG-DTA results. The oxides were characterized by adsorption–desorption isotherms of N<sub>2</sub> at 77 K, XRD, SAXS, solid-state <sup>13</sup>C CP/MAS NMR, FTIR, and SEM. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Mesoporous ZrO<sub>2</sub>; Sol–gel; Basic catalysis;  $C_nH_{2n+1}N(CH_3)_3Br$

### 1. Introduction

Since Stucky and coworkers [1] demonstrated that it was also possible to synthesize non-silica based mesostructured materials, an intense effort has been dedicated to such solids, with the niobium-, hafnium-, and cerium-based materials being the most frequently cited ones. Thermally stable mesoporous zirconium oxides were first prepared

by Ciesla et al. [2]. Many of the subsequent studies focused on the conditions that allow the synthesis of stable zirconium oxides. According to Pacheco et al. [3], and Huang et al. [4], the fixation of PO<sub>4</sub> or SO<sub>4</sub> on the walls may help to preserve the porous structure.

This study reports on the preparation of mesoporous zirconias synthesized under basic catalysis in the presence of a series of  $C_nH_{2n+1}N(CH_3)_3Br$ , with  $n = 8–18$ , as surfactants. The influence of some preparation parameters has been investigated, with consideration to the interaction between the quaternary salt and the inorganic matrix.

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## 2. Experimental

Mesoporous oxides were prepared via the sol-gel method using zirconium propoxide (ZP) as a precursor. The basic procedure was carried out using NaOH (pH > 11) or ammonia (pH = 10) as a catalyst. ZP in propanol was mixed with a propanol solution of the surfactant, with the base being added as an aqueous solution. The synthesis was performed using different Zr:H<sub>2</sub>O and Zr:surfactant molar ratios. The mixtures were heated under reflux at 363 K for one day. The sol-step and then the polymerization step were carried out at different temperatures. The samples were dried by: (i) lyophilization, (ii) in a vacuum oven at room temperature for 48 h, and (iii) in vacuum oven at 383 K for 48 h. Calcination of the materials was made on the basis of TG-DTA results. The samples were calcined in air at 653, 723 or 773 K for 10 h using a ramp of 0.2 K min<sup>-1</sup>. The oxides were characterized by thermal methods (TG-DTA), N<sub>2</sub> adsorption-desorption isotherms at 77 K, XRD, SAXS, <sup>1</sup>H and <sup>13</sup>C NMR, FTIR, and SEM.

Adsorption-desorption isotherms of N<sub>2</sub> were obtained with a Micromeritics ASAP 2000 apparatus after outgassing the samples at 443 K for 12 h. Thermal analyses were carried out using a SETARAM 92 16.18 equipment. The samples were heated between room temperature and 1053 K, at a heating rate of 10 K min<sup>-1</sup>. FTIR spectra were recorded with a Bruker FT-IR 88 spectrometer. Self-supported discs were obtained by compression of the powder with KBr (2 wt.% sample). The spectra were recorded after 30 scans for a resolution of 4 cm<sup>-1</sup>. XRD patterns of the samples were obtained with a Philips PW1050 diffractometer. Solid-state <sup>13</sup>C CP/MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer equipped with a double-bearing probe. SEM photographs were obtained with an ISI 60 apparatus combined with a PRODAS automatic storage system.

## 3. Results

### 3.1. Textural characteristics

The nitrogen adsorption-desorption isotherms are typical of mesoporous materials as illustrated

in Fig. 1 (Zr-10). Table 1 gives the textural characteristics of the zirconium oxides prepared under basic catalysis with, in regard, the corresponding Zr:H<sub>2</sub>O and Zr:surfactant molar ratios used at the synthesis step. The surface areas of these materials are smaller than the values generally reported in the literature. It is worth to note that the pore size distributions, except for a few samples, is multi-

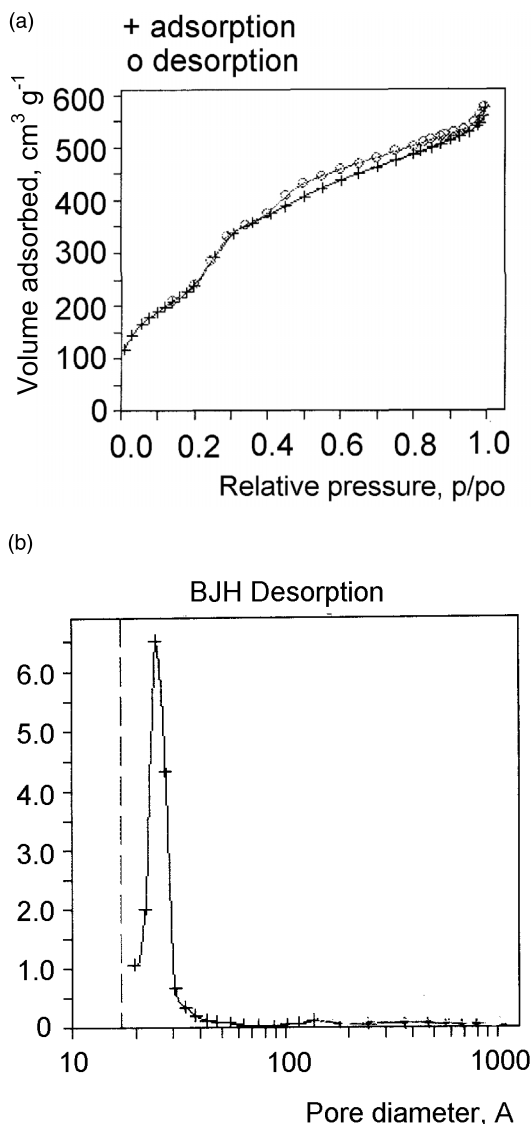


Fig. 1. (a) Adsorption-desorption isotherm and (b) pore size distribution of sample Zr-5.

Table 1  
Influence of the composition parameters on the texture

Sample	Surfactant	Zr/H <sub>2</sub> O	Zr/surfactant	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	BJH pore diameter (nm)
Zr-1 <sup>a</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1:1	1:1	2	2.0; 2.8 and over 40
Zr-2 <sup>a</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1:1	4:1	4	2.0; 2.8; 3.4 and over 40
Zr-3 <sup>a</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1:1	5:1	33	2.0; 2.8; 6.5 over 100
Zr-4 <sup>a</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1.5:1	4:1	123	2.8 and near 7
Zr-5 <sup>a</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	2.2:1	4:1	228	2.8
Zr-6 <sup>a</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	2.5:1	4:1	269	2.8
Zr-7 <sup>b</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>8</sub> H <sub>17</sub> Br	2.5:1	4:1	91	2.0; 2.7; 4.0
Zr-8 <sup>b</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>10</sub> H <sub>21</sub> Br	2.5:1	4:1	103	2.0; 2.7; 4.0
Zr-9 <sup>b</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>12</sub> H <sub>25</sub> Br	2.5:1	4:1	119	2.0; 2.7; 4.0
Zr-10 <sup>a</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>14</sub> H <sub>29</sub> Br	2.5:1	4:1	167	2.9
Zr-11 <sup>a</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>18</sub> H <sub>37</sub> Br	2.5:1	4:1	224	2.9; 4.6
Zr-12 <sup>b</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1.5:1	4:1	24	2.1; 2.8; 3.5; 32
Zr-13 <sup>c</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1.5:1	4:1	17	2.1; 2.8; 3.5; 32
Zr-14 <sup>d</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1.4:1	4:1	9	2.1; 2.8; 3.2; 4.0; 32
Zr-15 <sup>c</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1.4:1	4:1	10	2.1; 2.8; 3.2; 4.0; 32
Zr-15 <sup>f</sup>	N(CH <sub>3</sub> ) <sub>3</sub> C <sub>16</sub> H <sub>33</sub> Br	1.4:1	4:1	7	2.1; 2.8; 3.2; 4.0; 32

<sup>a</sup> Drying in air; rate 0.12 K min<sup>-1</sup>; 10 h at 383 K; calcination: in air; rate 0.12 K min<sup>-1</sup>; 6 h at 653 K.

<sup>b</sup> Drying in air; rate 0.12 K min<sup>-1</sup>; 10 h at 383 K; calcination: in air; rate 0.12 K min<sup>-1</sup>; 6 h at 773 K.

<sup>c</sup> Lyophilization; calcination: in air; rate 0.12 K min<sup>-1</sup>; 6 h at 653 K.

<sup>d</sup> Lyophilization; calcination: in air; rate 0.12 K min<sup>-1</sup>; 6 h at 773 K.

<sup>e</sup> Extraction in ethanol by percolation (363 K for 10 h); calcination: in air; rate 0.12 K min<sup>-1</sup>; 6 h at 653 K.

<sup>f</sup> Extraction in ethanol by percolation (363 K for 10 h); calcination: in air; rate 0.12 K min<sup>-1</sup>; 6 h at 773 K.

modal. However, except for the very small surface areas, the satellites have a small intensity.

The Zr:H<sub>2</sub>O molar ratio exerts a strong influence on the textural properties and appears to be the most important parameter. An increase of this ratio from 1:1 to 2.5:1 results both in an increase of the surface area, and a less dispersed distribution of the pore diameter. The maximum is centered at 2.7–2.9 nm, as a function of the length of the main chain in the surfactant. The Zr:surfactant molar ratio is another important parameter, with a low ratio (1:1) leading to solids with very small surface areas. The drying and calcination conditions constitute other key parameters. Smaller surface areas are obtained after calcination at 773 K compared with 653 K (Zr-7 vs Zr-8). TG-DTA measurements showed the occurrence of phase transformations above 623 K. Drying by lyophilization results in materials with small surface areas (compare Zr-7 and Zr-9). The chain length of the surfactant also has a marked influence on the textural characteristics, the highest surface area being obtained when using C16 (Zr-11). The extraction of the surfactant with ethanol from sam-

ples dried in a vacuum oven at room temperature followed by heating at 383 K and calcination does not improve the textural properties (Zr-5 and Zr-6). The extraction of the surfactant was carried out until the <sup>13</sup>C NMR signal of the surfactant was suppressed. This indicates that the surfactant should be kept in the material prior to the calcination.

### 3.2. XRD

The XRD analysis of the zirconium oxides indicates that, except for Zr-10 and Zr-11, for which the crystallographic structure corresponds to the tetragonal form (ASTM-17-0923), mixtures of the tetragonal and orthorhombic forms (ASTM-37-1413) [5] are produced (Fig. 2), in relative proportions depending on the molar ratios introduced at the preparation of these oxides. Low Zr:H<sub>2</sub>O and Zr:surfactant molar ratios result in an increase of the orthorhombic phase. The peaks located before 10° 2θ may indicate the existence of randomly oriented pores, whatever their organization is.

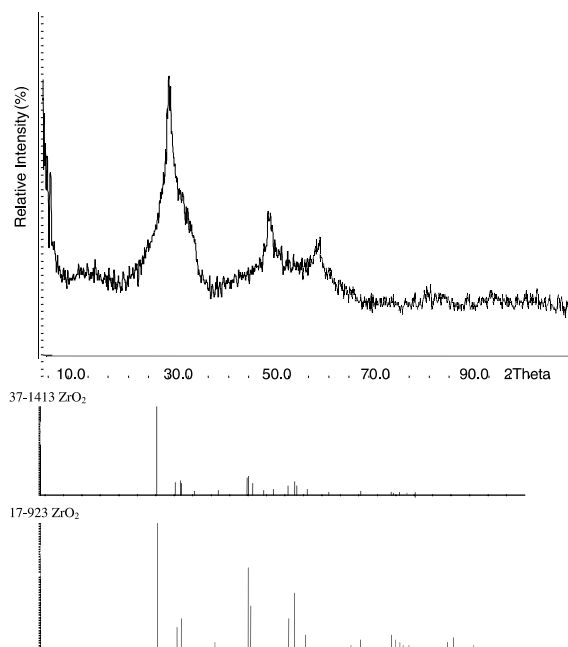


Fig. 2. XRD pattern of Zr-4 and of ZrO<sub>2</sub> (ASTM-37-1413 and ASTM-17-923).

### 3.3. SAXS

SAXS patterns of the ZrO<sub>2</sub> oxides exhibit a continuous decay without any peak, indicating the existence of a size controlled porosity. Fig. 3 shows the pattern obtained over Zr-10. The decay of the curves clearly demonstrates that the mesoporosity of these samples differs from that of the M41S materials. Although the pore size distributions of these samples exhibit roughly narrow shapes, several others causes, such as the tortuous shape of the pores or the random position with respect to each other, may contribute to this behavior.

### 3.4. FTIR

The FTIR analysis of the zirconium oxides confirms the results obtained with the other characterization techniques. The position of the bands located in the region 400–650 cm<sup>-1</sup> is consistent with the crystallographic structures identified by XRD (Fig. 4). The FTIR spectra recorded on

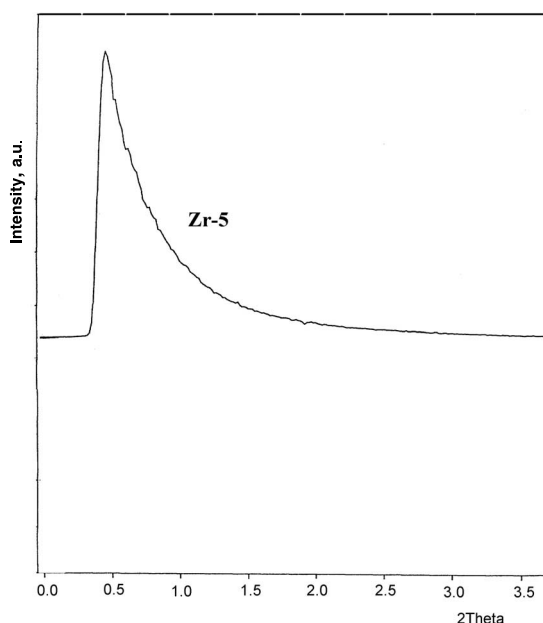


Fig. 3. SAXS of sample Zr-5.

dried samples show bands in the region 1500–1600 cm<sup>-1</sup>, corresponding to nitrogen containing species. No shift of the bands is observed with respect to those of the pure surfactant.

### 3.5. Solid-state <sup>13</sup>C CP/MAS NMR

Spectra recorded at several stages of the preparation and for dried samples show no interaction between the used template and the inorganic matrix. No shift of the position of the signals of the template indicative of an interaction with zirconia is noticed. Calcination of the catalysts leads to the decomposition of the surfactant and, at temperatures of 773 K, the organic part is almost totally eliminated [6].

### 3.6. SEM

Fig. 5 shows a SEM photograph of a mesoporous ZrO<sub>2</sub> (sample Zr-7) prepared according to the procedure indicated above. The micrograph clearly shows a porous texture, different from that of M41S-type materials.

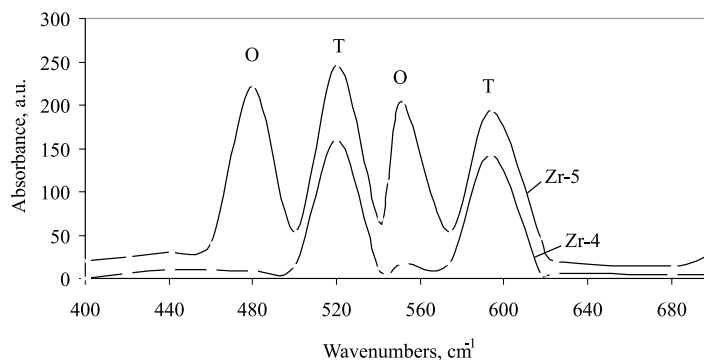


Fig. 4. FTIR spectra of Zr-4 and Zr-5. T-tetragonal, O-orthorhombic.

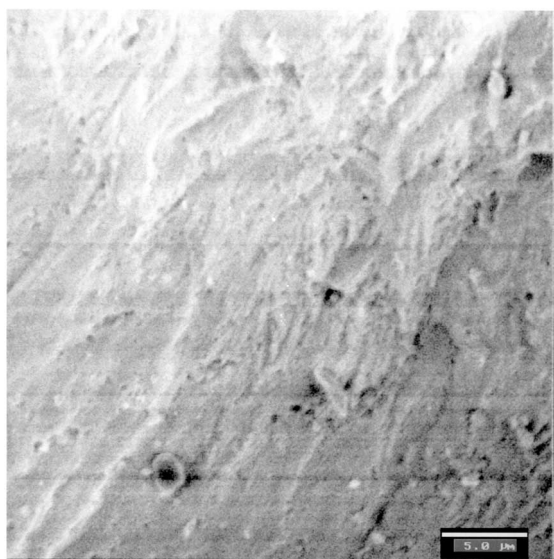


Fig. 5. SEM micrograph of Zr-4.

#### 4. Discussions

Sol-gel synthesis of  $\text{ZrO}_2$  oxides under basic conditions and in the presence of a series of surfactants of type:  $\text{C}_n\text{H}_{2n+1}\text{N}(\text{CH}_3)_3\text{Br}$  (with  $n = 8\text{--}18$ ) leads to mesoporous oxides. The adsorption-desorption isotherms are typical of such materials. But a careful examination of the pore size distribution shows that a monomodal pore distribution only occurs in a few cases, depending on the preparation parameters and type of surfactant. As

shown by SAXS and SEM analyses, these materials are mesoporous, but different from that of M41S materials. Both the tortuosity and random distribution of the pores in relation with each other cooperate to such a characteristics. The sol-gel procedure in basic conditions is very sensitive to the preparation parameters. The surface areas are smaller than those reported in the literature for acid-mediated preparation procedures [3,4].

From the structural point of view, these materials generally consist of a mixture of the tetragonal and orthorhombic phases. In very special conditions, it is possible to synthesize monophasic tetragonal oxides. But the different synthesis parameters have no influence on the coordination state of zirconium, as verified by XPS.

The contribution of the surfactant, and in particular the chain length, is essential. As established by NMR, no direct interaction between the surfactant and zirconium oxide occurs at the different preparation steps. The extraction of the surfactant prior to the thermal treatments causes a dramatic damage of the oxide structure and, as a consequence, materials with very small surface areas are obtained. This behavior is typical of a scaffolding mechanism, as it was previously suggested by Hudson and Knowles [7].

#### 5. Conclusions

The sol-gel synthesis of  $\text{ZrO}_2$  under basic catalysis and in the presence of  $\text{C}_n\text{H}_{2n+1}\text{N}(\text{CH}_3)_3\text{Br}$ ,

with  $n = 8$ –18, as surfactant, leads to mesoporous materials in which the surface area and the pore size distribution strongly depend on the preparation composition. The mesoporosity of these oxides, even when the pore size distribution is monomodal, corresponds to pores which exhibit some tortuosity. The phase structure is also dependent on the modification of the composition parameters.

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