Nanoporous zirconium oxide prepared using the supramolecular templating approach

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Hexagonal (Hx-ZrO_2) and lamellar (L-ZrO_2) phases of zirconium oxide have been prepared using the supramolecular templating approach. Long chain primary alkyl amines led to the formation of lamellar phases, while quaternary ammonium surfactants gave hexagonal phases. The materials have been characterized by XRD, TG/DTG, IR, XPS, SEM and EDX techniques. The influence of various synthesis parameters such as (i) the ZrO_2/surfactant ratio, (ii) the surfactant/water ratio, (iii) the nature of surfactant, (iv) the crystallization temperature and (v) the crystallization time have been investigated. The final solid products were found to be thermally unstable regardless of their structure. Removal of the surfactant from the mesopores by solvent extraction without damaging the structure was not possible.

Keywords: nanoporous zirconium oxide; supramolecular templating mechanism; hexagonal zirconium oxide; lamellar zirconium oxide

1. Introduction

The discovery of the liquid-crystal templating technique for the manufacture of M41S crystalline mesoporous materials [1] opened new opportunities in the design of innovative materials with potential use in catalysis [2], chemical sensing [3], data storage and other advanced applications [4]. Earlier investigations focused mainly on silicate and aluminosilicate MCM-41 molecular sieves [1,5]. An extensive series of inorganic metal oxides (W, Sb, Zn, Pb, Mg, Al, Mn, Fe, Co, Ni and Zn) with open-structure networks have also been reported [6]. These materials were prepared with both anionic and cationic surfactants. All oxides had a strong tendency to form lamellar phases. Exceptionally, W, Sb and Pb oxides gave hexagonal phases. The removal of the surfactant from the mesopores by solvent extraction techniques was unsuccessful and all phases collapsed after calcination regardless of their structure. Mallouk et al. [7] found that W, Nb, V and Mo oxide precursors tend to form stable unconnected Keggin ions instead of condensed frameworks. Recently, we extended this synthesis technique to aluminophosphates [8].

Surfated zirconia is a strongly acidic catalyst with potential applications in hydrocracking and hydroisomerization [9]. These catalysts have surface areas of about 70–100 m^2/g. If this surface area could be increased to ca. 1000 m^2/g, typical of mesoporous molecular sieves, it would improve the likelihood of commercial applications of sulfated zirconia. This has prompted us to prepare mesoporous zirconium oxide using the liquid crystal templating approach. In this paper, for the first time, we report data on the preparation and characterization of hexagonal (Hx-ZrO_2) as well as lamellar (L-ZrO_2) mesophases of zirconium oxide. Long chain alkyltrimethyl quaternary ammonium salts and primary amines, were used as supramolecular structure directing agents.

2. Experimental

Hx-ZrO_2 and L-ZrO_2 phases were prepared using two different methods (A and B). Table 1 summarizes the molar gel compositions of these materials.

Method A: An aqueous solution of zirconium sulfate was added to cetyltrimethylammonium bromide (CTMA-Br) dissolved in water. The pH of the final reaction mixture was about 1.0. This mixture was autoclaved at different temperatures for 10 min to 5 days.

Method B: The desired amount of 1 N HCl solution as indicated in table 1 was added to dodecylamine in water. After stirring this mixture for 5 min, a zirconium sulfate solution was added under vigorous stirring. The final reaction mixture thus obtained (pH = 0.9) was stirred for 30 min and then kept at room temperature or at 373 K under static conditions. Some L-ZrO_2 samples were prepared using the same procedure except that 2/3 of HCl was replaced by H_2SO_4. The pH of this gel was about 0.7. In one synthesis (sample No. 20, table 1), ethanol was added to the template instead of water.

After crystallization, all the products were filtered, washed thoroughly with water, then with ethanol, and dried at ambient temperature.

Characterization techniques included XRD (Siemens 5000 diffractometer), FTIR (Nicolet 550 spectrometer

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Table 1
Gel composition and properties of zirconium oxide mesophases

Sample No.[a]	C_nH_{2n+1}– n =	Gel composition					Cryst. temp. (K)	Cryst. time (h)	Final phase	d-spacing (Å)
		ZrO_2	R[b]	HCl	H_2SO_4	H_2O				
1(A)	16	1.0	0.27	–	–	60	373	48	Hx	43.3
2(A)	16	1.0	0.27	–	–	60	300	0.5	Hx	41.2
3(A)	16	1.0	0.13	–	–	60	373	48	Hx	42.4
4(A)	16	1.0	0.54	–	–	60	373	48	Hx	38.3
5(A)	16	1.0	1.08	–	–	60	373	48	Hx	42.8
6(A)	16	1.0	0.13	–	–	30	373	48	Hx	40.7
7(A)	16	1.0	0.54	–	–	120	373	48	Hx	39.4
8(A)	16	1.0	1.08	–	–	240	373	48	Hx	39.7
9(A)	8	1.0	0.27	–	–	60	373	48	none	–
10(A)	12	1.0	0.27	–	–	60	373	48	none	–
11(A)	14	1.0	0.27	–	–	60	373	48	Hx	37.4
12(B)	12	1.0	0.27	–	–	60	300	0.5	L	33.7
13(B)	12	1.0	0.27	–	–	60	373	48	L	35.3
14(B)	8	1.0	1.04	1.13	–	375	300	24	none	–
15(B)	10	1.0	1.04	1.13	–	375	300	24	none	–
16(B)	16	1.0	1.04	1.13	–	375	300	24	L	43.3
17(B)	12	1.0	1.04	0.3	1.0	375	300	24	L	34.2
18(B)	12	1.0	2.08	0.3	1.0	375	300	24	L	34.5 (25.4[c])
19(B)	12	0	0.27	0.3	1.0	375	300	24	L	25.1
20(B)	12	1.0	0.27	17 Et-OH		60	300	24	L	32.2

[a] The letter in parentheses indicates the method employed to prepare the material.
[b] R = template.
[c] Impurity of a phase similar to sample No. 19.

using the KBr pellet technique), XPS (V.G. Scientific Escalab Mark II system), scanning electron microscopy (JEOL 840A) and energy dispersive X-ray (EDX) analysis.

3. Results and discussion

There is a broad consensus that the synthesis of mesoporous materials in the presence of surfactant molecules takes place according to a cooperative mechanism [10]. The cornerstone of this mechanism is that the inorganic charged species in the synthesis mixture play a major role in determining the nature of the mesophase. Based on a number of convincing arguments, it was shown that the existence of a preorganized liquid-crystal surfactant phase is not required for the formation of an organic–inorganic mesophase. These arguments were (i) MCM-41 could be synthesized with 1 wt% surfactant (with respect to water content), which is well below the critical concentration for the formation of rod-like micelles (cmc2), (ii) MCM-41 was prepared using short chain surfactants such as C_8TMA-X, C_{12}TMA-X (X = Cl^- or Br^-), for which no rod-like micelles were reported to form in aqueous solutions, and (iii) the synthesis of MCM-41 was achieved at high temperatures, where the stability of rod-like micelles is very low.

According to this mechanism, the organization of individual surfactant molecules into various organic array configurations is governed by their electrostatic interaction with polydentate and polycharged molecular inorganic species. The charge and the geometry of inorganic species in solution is governed in addition to their concentration by pH, cosolvent, counterions and reaction temperature. The ion-pairs formed between polycharged inorganic species and the surfactant organize into liquid-crystal-like array, and finally the condensation of inorganic species takes place.

This so-called cooperative mechanism has been substantiated by applying this strategy to the preparation of various mesoporous structures using cationic, anionic or zwitterionic surfactants under conditions where cationic, anionic or neutral inorganic species are formed. These synthesis strategies were classified into five different pathways [10,11]. In pathway 1 referred to as (S^+I^-), the co-operative assembly of anionic inorganic silicate species and cationic surfactant occurs, while in pathway 2 (S^-I^+) the opposite situation prevails, i.e. formation of cationic inorganic silicate species and anionic surfactant ion pairs. In pathways 3 ($S^+X^-I^+$; X = F^-, Cl^-, Br^-, etc.) and 4 ($S^-M^+I^-$; M = Na^+, K^+, etc.), the condensation of similarly charged inorganic and surfactant species takes place with the mediation of ions with the opposite charge. In pathway 5 (S^0I^0) the interaction occurs between neutral silicate species and neutral surfactant.

In the synthesis of ZrO_2 mesophases, because of the use of a strongly acidic zirconium source, the pH of the synthesis gel was always below 1.5. Therefore, even when primary amines were used, they were actually protonated. According to the aqueous chemistry of zirconium, at very low pH, though there are no convincing data to prove the presence of monomeric ZrO^{2+} [12], some studies indicated the occurrence of tetranuclear $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ions [13,14]. The extent of polymerization depends on the concentration of zirconium solution and the pH [15]. As in the case of MCM-41 silicate, the main driving force for the formation of ZrO_2 mesophases in strong acid media must be due to electrostatic interactions between cationic zirconium species and cationic surfactant head groups, probably mediated by the sulfate (SO_4^{2-}) ions. Using the XPS technique we found that there were no Br^- ions in the hexagonal phase (sample No.1), which indicates that Br^- ions are not mediating the cooperative assembly. However, the Zr/S ratios of hexagonal (sample No. 1) and lamellar (sample No. 13) phases were 1.3 and 1.1, respectively. Similar observations were made by EDX, even though the Zr/S ratios were somewhat lower (ca. 0.9). Based on these results, we classify the synthesis of Hx-ZrO_2 and L-ZrO_2 to pathway 3, with SO_4^{2-} as the mediating anion.

Scanning electron microscopy showed that both materials appear as shapeless aggregated particles.

When the source of zirconium ($Zr(SO_4)_2$) was replaced by zirconium isopropoxide, $Zr(Oi\text{-}C_3H_7)_4$, the pH of the gel was about 5.0. At this pH, zirconium oxide was formed and the resultant material was amorphous.

The influence of various synthesis parameters like (i) the ZrO_2/surfactant ratio, (ii) the surfactant/water ratio, (iii) the nature of surfactant, (iv) the crystallization temperature and (v) the crystallization time was investigated. The results are reported in table 1. Representative XRD patterns of hexagonal and lamellar phases are shown in fig. 1. Samples prepared using method A had XRD patterns typical to MCM-41 hexagonal phase. The occurrence of lamellar phases was revealed by the presence of multiple peaks that are higher orders of the first (001) peak.

As in the case of hexagonal and lamellar silicate mesoporous molecular sieves [1], the increase in the carbon chain length of the surfactant increases the *d*-spacing of both hexagonal and lamellar phases of ZrO_2. With the same number of carbon atoms in the alkyl chain, both Hx-ZrO_2 and L-ZrO_2 had similar *d*-spacings (fig. 1). Contrary to MCM-41 silicates, primary amines and quaternary ammonium salts with alkyl chain length of less than 10 and 12 carbon atoms, respectively did not yield any ZrO_2 mesophase. Unlike quaternary ammonium surfactants, under our synthesis conditions, the use of primary amine surfactants led to the exclusive formation of lamellar phases of zirconium oxide.

XRD patterns of Hx-ZrO_2 samples prepared using different CTMA-Br/ZrO_2 ratios and a constant ZrO_2/H_2O ratio are plotted in fig. 2 (curves A–D). To keep the total concentration of surfactant in water constant, we have also prepared a series of samples with different CTMA-Br/ZrO_2 ratios while keeping the CTMA-Br/H_2O ratio equal to 60 and varying the water content (ZrO_2/H_2O ratio). Contrary to the M41S silicate mate-

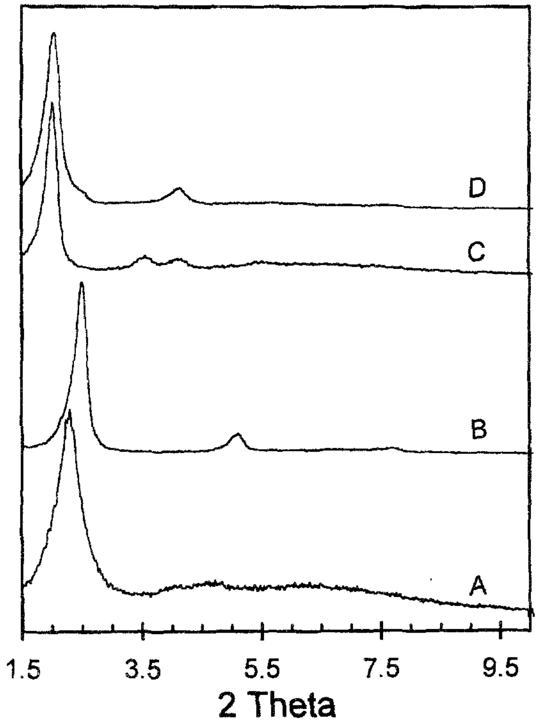

Fig. 1. XRD patterns of Hx-ZrO_2 (A and C) and L-ZrO_2 phases (B and D) prepared in the presence of surfactants of different chain lengths. (A) $C_{14}H_{29}(CH_3)_3NBr$ (sample No. 11), (B) $C_{12}H_{25}NH_2$ (sample No. 13), (C) $C_{16}H_{33}(CH_3)_3NBr$ (sample No. 1) and (D) $C_{16}H_{33}NH_2$ (sample No. 16).

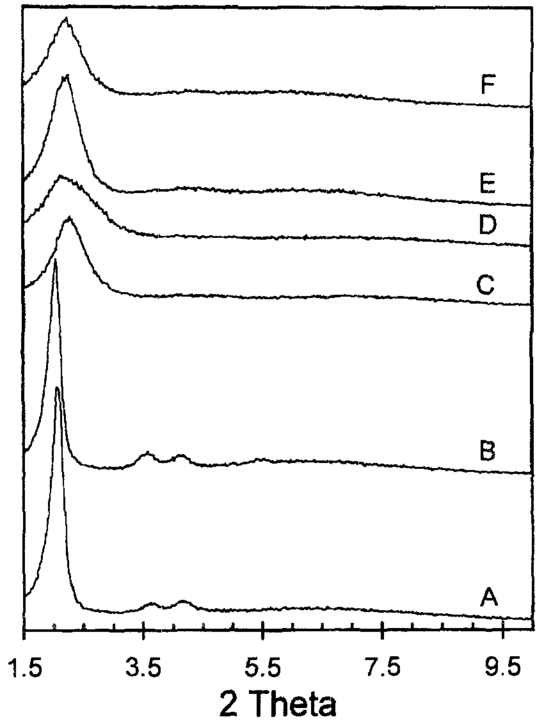

Fig. 2. XRD patterns of Hx-ZrO_2 samples prepared at different $C_{16}H_{33}(CH_3)_3NBr$/ ZrO_2 (A, B, C and D) and $C_{16}H_{33}(CH_3)_3NBr$/ water (E and F) ratios. Diffractograms (A–F) correspond to samples Nos. 3, 1, 4, 5, 6 and 8, respectively.

rials, in the presence of quaternary ammonium surfactants, even at high surfactant to Zr ratios (> 1), only hexagonal phases were obtained. Samples obtained with surfactant/ZrO_2 ratios of 1.08 and 0.54 had a typical XRD pattern of the hexagonal MCM-41 structure, with distinct (110) and (200) peaks, in addition to the intense (100) peak. However, at higher ratios only the lowest angle (100) peak was observed. Based on earlier investigations on silica M41S molecular sieves, the absence of higher order Bragg reflections in these samples can be attributed to a diminishing order of the mesoporous system [16]. At higher surfactant/ZrO_2 ratios, the higher amounts of water added to keep the surfactant/H_2O ratio constant had a negligible effect on the product obtained (fig. 2; curves E and F).

Both lamellar and hexagonal phases could be prepared at room temperature within short reaction times. The XRD spectra of hexagonal samples prepared in the presence of CTMA-Br at 300 and 373 K for different periods of time are plotted in fig. 3. Longer crystallization times and higher temperatures favor the formation of materials with well defined (110) and (200) XRD peaks at $2\theta = 3.6°$ and 4.2°, respectively. However, for much longer reaction times (ca. 5 days), at 373 K, a new phase began to develop. Likewise, the XRD spectra of L-ZrO_2 improved when the samples were prepared at 373 K instead of 300 K (figs. 3A and 3B).

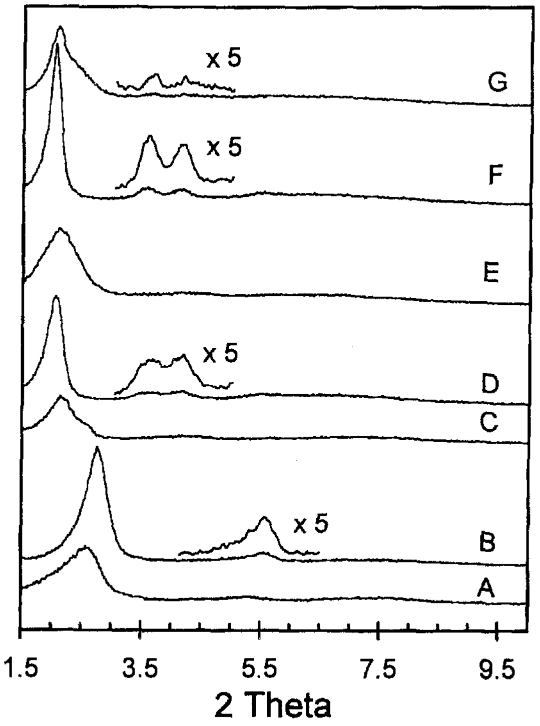

Fig. 3. XRD patterns of Hx-ZrO_2 and L-ZrO_2 samples prepared at different temperatures during different periods of time. Diffractograms (A) and (B) correspond to L-ZrO_2 samples prepared at 300 and 373 K, respectively. Diffractograms (C) and (D) belong to sample No. 2 prepared in 10 min and 24 h, respectively. Diffractograms (E, F, G) represent sample No. 1 after 1, 2 and 5 days of crystallization.

Thermogravimetric data of both lamellar and hexagonal phases are shown in fig. 4. The total weight loss for Hx-ZrO_2 and L-ZrO_2 was 68 and 75 wt%, respectively. The surfactant in L-ZrO_2 decomposes in one stage, while in Hx-ZrO_2, it decomposes at least at two different temperatures. The decomposition at 520°C may be due to the surfactant trapped in between the collapsed ZrO_2 pore walls. The initial decrease in the weight below 423 K corresponds to the loss of water.

Calcination of lamellar as well as hexagonal materials at 773 K for 6 h resulted in a structural collapse. For M41S silicates prepared via pathways 3, 4 and 5, the surfactant was removed by mere refluxing in a solvent. In pathways 3 and 4, inorganic anions or cations compensate the wall charge, so that the surfactant can be easily removed. In the case of ZrO_2 mesophases, the charge on the ZrO_2 wall is also compensated by sulfate ions. Therefore it should be possible to extract the surfactant without the loss in the mesoporous structure. However, treatment of Hx-ZrO_2 samples under refluxing conditions in various solvents like acetone, ethanol and ethanol–*n*-heptane mixture led to the extraction of only negligible amounts of surfactant. Nevertheless, in the presence of ethanol–*n*-heptane–HCl mixture as suggested in the patent literature [17], all the surfactant present in the mesopores of Hx-ZrO_2 was extracted. The disappearance of C–H vibrations in the FTIR spectrum of the sample after the treatment strongly supports this conclusion. However, the material became amorphous with almost no porosity, indicating that the template free Hx-ZrO_2 is inherently unstable.

According to literature data, the lamellar silica phase is also thermally unstable under calcination conditions.

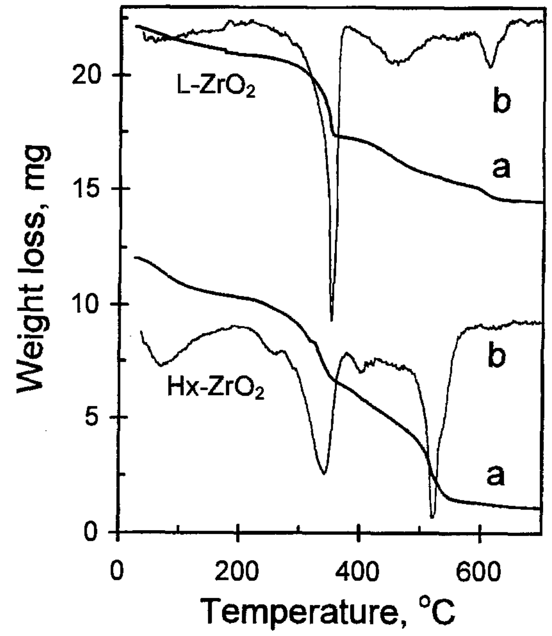

Fig. 4. Thermogravimetric data of Hx-ZrO_2 (sample No. 1) and L-ZrO_2 (sample No. 13) phases; (a) TGA; (b) first derivative of TGA curve.

It can be stabilized by treating with inorganic alkoxides like tetraethylorthosilicate (TEOS) [18]. Unfortunately, none of the ZrO_2 mesophases could be stabilized using this technique.

4. Conclusions

The liquid-crystal templating approach has been used to prepare open framework structures of zirconium oxide. We have demonstrated that by choosing proper synthesis conditions, hexagonal or lamellar phases of zirconium oxide could be prepared. Both phases collapsed under calcination conditions. The hexagonal structure also collapsed upon removal of the surfactant by solvent extraction.

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