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Synthesis of Stable Mesostructured Zirconia: Tween Surfactant and Controlled Template Removal

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Abstract−Mesostructured zirconia has been synthesized by using zirconium chloride and PEO nonionic ethoxylated sorbitan ester (Tween-20, -40, -60 or -80) as a zirconium source and structure-directing agent in an aqueous medium. To remove the occluded surfactants, UV/ozone treatment has been utilized instead of calcination due to thermal instability. This results from a special molecular structure of Tween surfactant. From XRD, SEM and TEM analyses, the materials treated with UV light and in-situ generated ozone has a wormhole structure and ill-defined or well-defined spherical particles.

Key words: Zirconia, Surfactant, Tween, Mesostructured, UV/Ozone, Wormhole

INTRODUCTION

Since the discovery of mesoporous silicates based on amphiphilic supramolecular templates [Kresge et al., 1992; Inagaki et al., 1993], this surfactant templating procedure has been extended to the formation of non-silica mesoporous oxides such as titania [Antonelli and Ying, 1995], niobia [Antonelli and Ying, 1996], tantala [Antonelli and Ying, 1996], alumina [Bagshaw and Pinnavaia, 1996; Kim et al., 2002], manganese oxide [Tian et al., 1997], hafnia [Liu et al., 1997] and zirconia. Among these non-silica oxides, zirconium oxide is of particular interest for acid catalysis [Sohn et al., 1987; Yamaguchi, 1994]. Hence, much effort has been directed to the preparation of mesoporous zirconia using cationic quaternary ammonium [Ciesla et al., 1999; Reddy and Sayari, 1996; Knowles and Hudson, 1995], anionic surfactants [Wong and Ying, 1998; Pacheco et al., 1997] and primary amines [Huang et al., 1996] as the structure directing agents. Yang et al. [1998, 1999] recently prepared mesoporous ZrO_2 using block copolymers and zirconium chloride in a nonaqueous medium. This material was reported to have two-dimensional (2D) hexagonal structure with a semicrystalline wall. They utilized inorganic salts as metal precursors in a nonaqueous medium such as ethanol solution, because the presence of water makes the hydrolysis and condensation of reactive metal species as well as the subsequent mesostructure assembly difficult to control [Vioux, 1997].

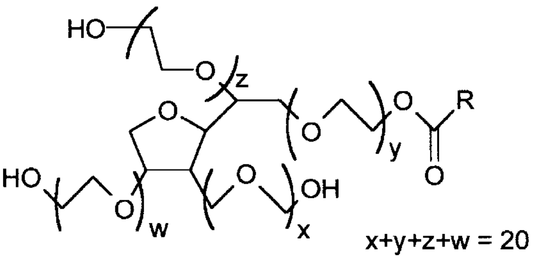
In recent years, mesoporous silica molecular sieves were prepared in the presence of nonionic poly(ethylene oxide) (PEO) based surfactants. These materials were named as MSU-X (X=1 to 4) (MSU for Michigan State University) where X refers to the surfactant molecules that can be either alkyl-PEO, alkyl-aryl PEO, PEO-PPO-PEO block copolymers, or ethoxylated derivatives of the fatty esters of sorbitan (Tween), respectively [Bagshaw et al., 1995; Prouzet et al., 1999]. The MSU-X compounds usually prepared in neutral pH possess a 3D wormhole porous framework with poor crystallographic symmetry, which is expected to enhance the diffusion rate of reacting species.

In this study, PEO nonionic surfactant Tween is used as the structure-directing agent. The zirconium mesophase is prepared in an aqueous medium in contrast to the work of Yang et al. [1998, 1999] and is treated with ultraviolet (UV) light and in-situ generated ozone instead of calcination. Finally, the material obtained in this work is compared to the one synthesized in a nonaqueous medium.

EXPERIMENTAL

1. Preparation of Zirconium Mesophase

The zirconium mesophase was synthesized by using the ethoxylated derivatives of the fatty esters of sorbitan, called Tween, as the structure-directing agent. There is a series of Tween surfactants with different hydrophobic chains, abbreviated as Tw-*X* where *X* is 20, 40, 60 or 80. The structure of Tw-*X* is depicted in Fig. 1. In a typical preparation, 0.002 mol of Tw-*X* was dissolved in 100 g of water. To this solution, zirconium chloride precursor in anhydrous ethanol



Tween 20: Polyoxyethylene sorbitan monolaurate (R: $C_{11}H_{23}$)
Tween 40: Polyoxyethylene sorbitan monopalmitate (R: $C_{15}H_{31}$)
Tween 60: Polyoxyethylene sorbitan monostearate (R: $C_{17}H_{35}$)
Tween 80: Polyoxyethylene sorbitan monooleate (R: $C_7H_{14}CH=CHC_8H_{17}$)

Fig. 1. Structure of the ethoxylated sorbitan Tween surfactants.

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(10 mL) was added slowly under vigorous stirring, where Zr/surfactant molar ratio was equal to 8. The mixture was then stirred continuously in a thermostatic oil bath maintained at 100 °C for 48 hr. The powder obtained was filtered, washed with ethanol and dried at room temperature.

2. Removal of PEO Nonionic Surfactant

The zirconium mesophase was found to be thermally unstable because calcination at 500 °C leads to a structure collapse, resulting in the black compound. Instead of calcination, the material was treated with UV light and in-situ generated ozone at room temperature to remove the occluded surfactants. Recent studies have suggested that UV/ozone treatment is an effective method for the removal of the template surfactants from bulk 3D MCM-41 materials [Keene et al., 1998] or 2D mesoporous thin films [Clark Jr. et al., 2000]. In a typical treatment, the dried zirconium mesophase was placed on a watch glass and then exposed to UV light (λ=184-257 nm) generated by a low-pressure Hg discharge lamp (electrical power 20 W) in a quartz envelope. This treatment was carried out within a closed chamber stored in a fume hood for an appropriate period of time.

3. Characterization of Mesostructured Zirconia

Powder X-ray diffraction patterns in the 2θ range of 1-10° were collected at ambient temperature by using Cu-Kα radiation, λ= 1.54056 Å, on a Philips X'Pert MPD diffractometer operating at 40 kV and 40 mA. Transmission electron microscopy (TEM) studies were performed on a JEOL JSM-2000EXII electron microscope operating at 200 keV. The samples for TEM were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions. Field emission scanning electron microscopy (FE-SEM) was performed on a JEOL JSM-6700F microscope. Fourier transform infrared spectroscopy (FT-IR) was utilized to confirm the complete removal of the surfactants on a Nicolet Impact 410. The sample was dispersed in KBr (sample/KBr=1/100 weight ratio) and pressed to wafer.

RESULTS

Fig. 2 shows the FT-IR spectra of a zirconium mesophase and samples treated with UV/ozone for different periods of time. The peaks assigned to C-H stretching (2,924 and 2,854 cm^{-1}) were observed in the former, whereas they tended to disappear as the exposure time to UV light increases. After 5 hr of UV/ozone treatment, the C-H peaks were no longer observed, indicating that the surfactant was completely removed. Tw-*X* templated materials, which were treated with UV light and in-situ generated ozone for more than 5 hr, will be designated as Tw-*X*–ZrO$_2$.

Fig. 3 shows the XRD patterns for the zirconium mesophases prepared with a series of Tween surfactants. The patterns resemble those obtained for MSU-X silicas with a single correlation peak [Bagshaw et al., 1995; Prouzet et al., 1999]. This single peak pattern is typical of materials possessing the 3D wormhole porous framework structure. A broad peak is also observed near 2θ of 5°. Analyses are in progress to identify this second diffraction feature, which cannot be assigned to a disordered hexagonal framework but could be related to the wormhole geometry of the porous framework. Fig. 4 presents the XRD patterns for Tw-*X*–ZrO$_2$ (*X*=20, 40, 60 and 80). The XRD patterns of UV/ozone-treated samples are very similar to those of the corresponding zirconium mesophases.

Table 1 summarizes the maximum 2θ of the peak observed in the XRD patterns of the zirconium mesophases and UV/ozone-treated samples, and their corresponding *d* spacing. In comparison between the two samples, the latter has a larger 2θ value and thus a smaller *d* spacing than the former. This indicates that UV/ozone treatment leads to the shrinkage of pores. In both the zirconium mesophases and UV/ozone-treated samples, the *d* spacing increases from 3.20 to 3.66 nm and 2.88 to 3.55 nm, respectively, as the length of hy-

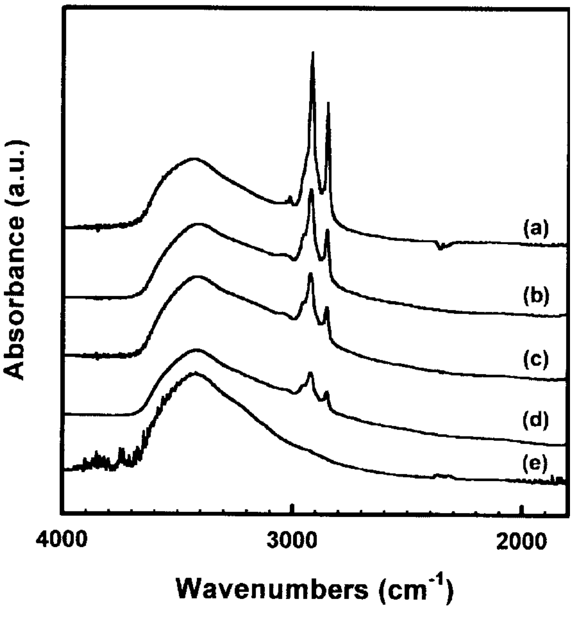

Fig. 2. FT-IR spectra of (a) a zirconium mesophase and samples treated with UV light and in-situ generated ozone for (b) 1 hr, (c) 2 hr, (d) 3 hr and (e) 5 hr.

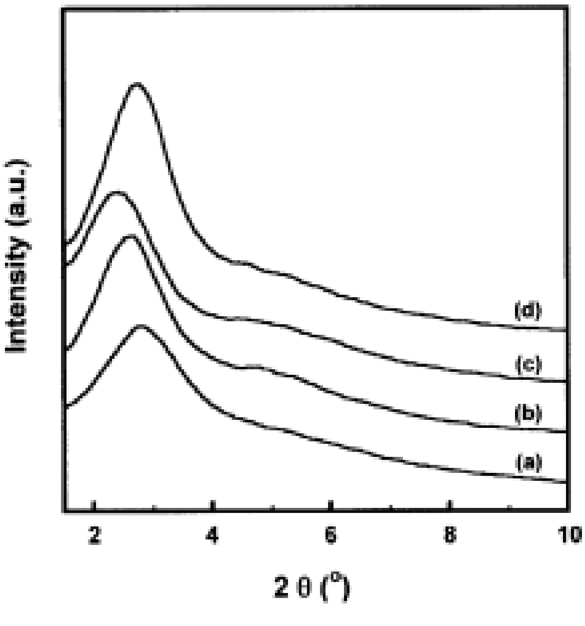

Fig. 3. XRD patterns of zirconium mesophases prepared with a series of Tween surfactants; (a) Tw-20, (b) Tw-40, (c) Tw-60 and (d) Tw-80.

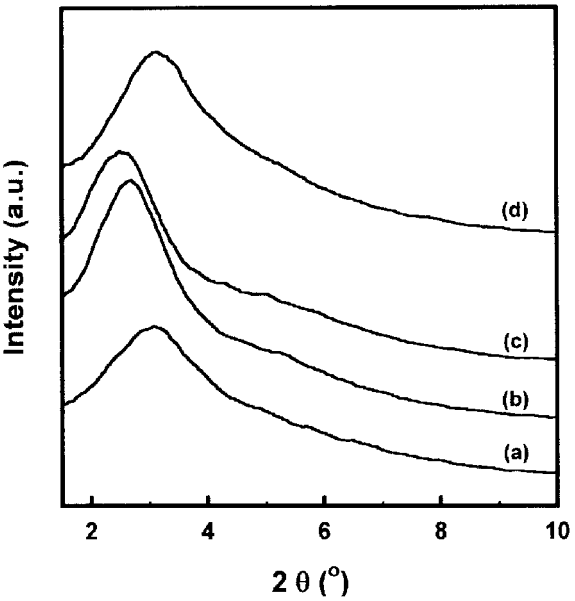

Fig. 4. XRD patterns of UV/ozone-treated Tw-*X*–ZrO_2; *X*=(a) 20, (b) 40, (c) 60 and (d) 80.

Table 1. Values of 2θ and the corresponding *d* spacing observed in the XRD patterns of zirconium mesophases and UV/ozone-treated samples prepared with a series of Tween surfactants

Surfactant	Zirconium mesophase		UV/ozone-treated sample	
	2θ (°)	*d* spacing (nm)	2θ (o)	*d* spacing (nm)
Tw-20	2.76	3.20	3.06	2.88
Tw-40	2.66	3.32	2.69	3.28
Tw-60	2.41	3.66	2.49	3.55
Tw-80	2.76	3.20	3.14	2.81

drophobic chains increases from Tw-20 (R=$C_{11}H_{23}$) to Tw-60 (R=$C_{17}H_{35}$). Surprisingly, Tw-80 with an unsaturated $C_{17}H_{33}$ chain (see Fig. 1) results in a pore size reduction compared to Tw-40 and Tw-60. Therefore, the normally observed correlation between the hydrophobic chain length and the *d* spacing does not apply in this case [Beck et al., 1994]. This result is similar to those observed in MSU-4 silicas [Prouzet et al., 1999].

SEM images showing the particle texture of Tw-*X*–ZrO_2 (*X*=20, 40, 60 and 80) are displayed in Fig. 5. Tw-20 provides a zirconia

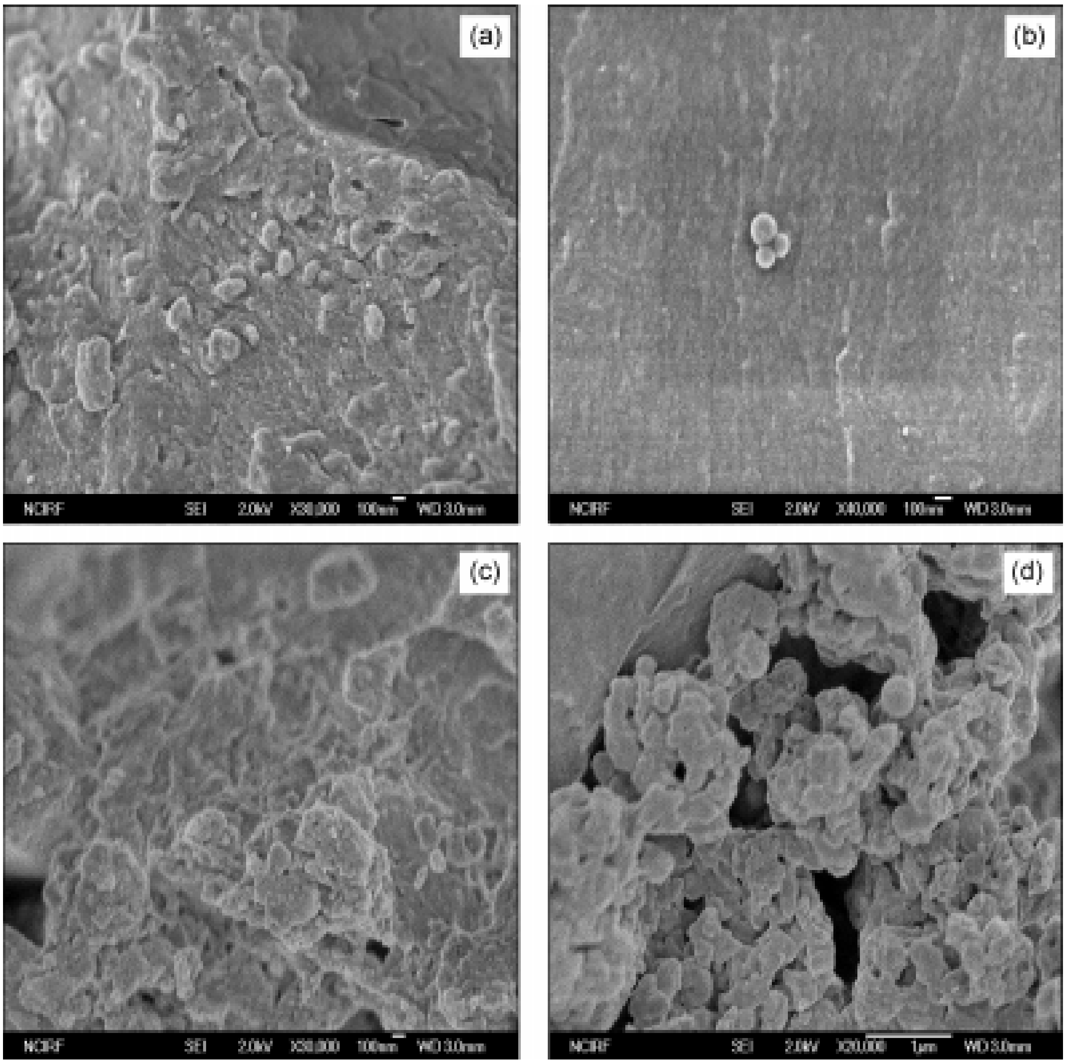

Fig. 5. SEM images of UV/ozone-treated Tw-*X*–ZrO_2; *X*=(a) 20, (b) 40, (c) 60 and (d) 80.

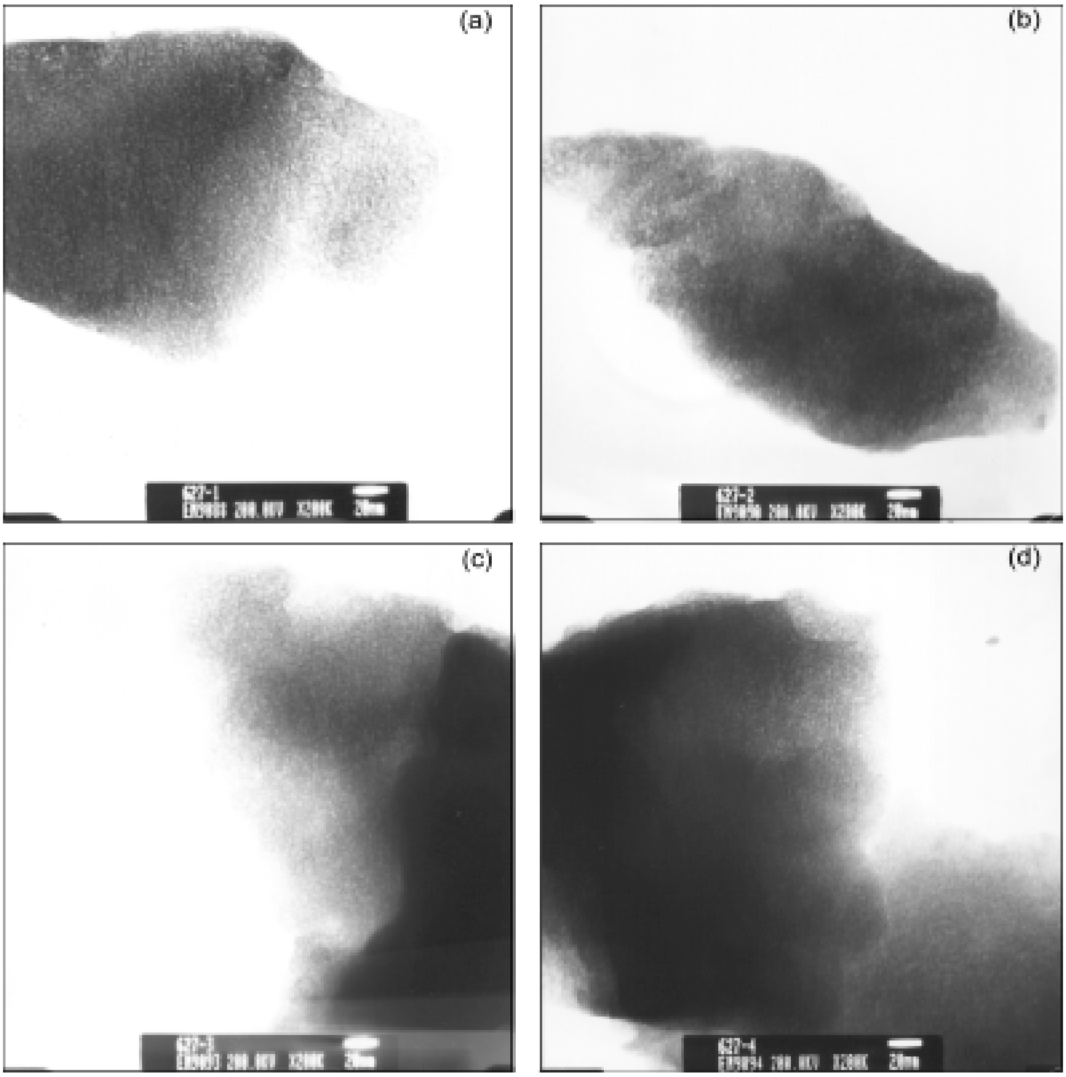

Fig. 6. TEM images of UV/ozone-treated Tw-X–ZrO$_2$; X=(a) 20, (b) 40, (c) 60 and (d) 80.

with ill-defined spherical particles whereas Tw-40 yields a zirconia with well-defined elementary spherical particles with a mean diameter of 150 nm. Unlike Tw-20 and Tw-40, the materials synthesized with Tw-60 and Tw-80 exhibit a structure with large aggregates of about 0.5 and 1 μm, respectively, consisting of small and ill-defined particles. These particles are much smaller than those usually obtained with MCM-41-type materials having a mean diameter of ~2 μm [Kresge et al., 1992]. Therefore, it is expected to obtain a textural porosity.

TEM images of UV/ozone-treated Tw-X–ZrO$_2$ (X=20, 40, 60 and 80) are shown in Fig. 6. It is noticed that no apparent order exists in the pore arrangement, which is in good agreement with the absence of extra peaks in the XRD patterns. All the zirconia samples prepared with Tween surfactants exhibit a framework with 3D wormhole pore structure. Similar pore distributions were observed in MSU-X silicas [Bagshaw et al., 1995; Prouzet et al., 1999] and aluminas [Bagshaw and Pinnavaia, 1996].

DISCUSSION

In general, the self-assembly of MSU-X silicas occurs in a near-neutral pH range that corresponds to the lowest reactivity domain for TEOS hydrolysis. Especially, MSU-4 silica can be synthesized by the addition of fluoride ion, acting as a mineralizer that boosts the reaction rate and improves the structural quality of the final material without changing the pH of the solution [Prouzet et al., 1999]. However, the present zirconium mesophase has been synthesized without NaF addition at a low pH of ~1, which was due to chlorine ions of zirconium source. This environment is the same as the one reported by Yang et al. [1998, 1999]. They suggested that the assembly mechanism uses the PEO-metal complexation, in conjunction with electrostatic, hydrogen bonding and van der Waals forces to direct the mesostructure formation. It is, therefore, considered that these interactions may also be utilized in the zirconium mesophase prepared with Tween surfactants in this work.

However, there is a difference between the synthesis condition reported by Yang et al. [1998, 1999] and the present one. In other words, the present zirconium mesophase was prepared in an aqueous medium. In fact, the hydrolysis and condensation of inorganic precursors must be important in the formation of mesophases for most of the non-silica oxides. Because of the lower electronegativities of the transition metal compared to silicon [Livage et al., 1988], their alkoxides undergo nucleophilic reactions such as hydrolysis and condensation more readily. This results in a precipitation and crystallization into bulk oxide phases directly in aqueous media. Such a phenomenon was not observed when zirconium chloride solution was mixed with the aqueous solution of Tween surfactants.

After the mixture was placed at 100 °C, it was at last changed to a milky emulsion, which indicates that the hydrolysis as well as the self-assembly is retarded under the present condition. This is evidently caused by Tween surfactants used as the structure-directing agent. In the mesoscopically ordered inorganic/copolymer composites prepared by Yang et al. [1998, 1999], alkylene oxide segments can form crown-ether-type complexes with many inorganic ions through weak coordination bonds, leading to an inorganic amorphous wall structure. During subsequent calcination, the thick walls and noncrystallized matrix prevent the mesostructures from collapsing. Tween surfactants used in this work, however, have a very special molecular structure as will be discussed below. Therefore, the present zirconium mesophase has a thin inorganic wall. This finally results in a structural collapse during calcination. Hence, we adopted the UV/ozone treatment instead of calcination to remove the occluded surfactants. Also, nitrogen adsorption/desorption analysis could not be performed because the samples should be pretreated at high temperature under vacuum before the analysis.

It is usually expected that change in the length of the hydrophobic chain of the surfactant allows one to modify the pore size of the final mesostructure. This feature, which is usually observed in most of the mesostructure syntheses, does not seem to hold for ethoxylated sorbitan structure directors. Tween surfactants have a very special shape with a short hydrophobic chain compared to a large hydrophilic head consisting of three free PEO chains and another one linking the ring to the hydrophobic tail, as shown in Fig. 1. When aggregated into micelles, these molecules most likely have their free PEO chains oriented in parallel as much as possible with the alkyl tail, so that a short hydrophilic shell around the hydrophobic core may be formed [Prouzet et al., 1999]. The binding of silica to the hydrophilic shell may alter the geometrical parameters, thus causing the pore size not to scale directly in proportion to the surfactant chain length.

On the other hand, hexagonal M41S silicates are formed under the reaction conditions in which silicate anions are bound electrostatically to segregated rod-shaped micelles of quaternary ammonium ions that subsequently aggregate into a mesostructure. An analogous assembly mechanism most likely operates for templating by nonionic PEO micelles. However, the micelles formed in the presence of $Si(OC_2H_5)_{4-x}(OH)_x$ precursors are more worm-like than rod-like and the precursors are bound to the flexible micelles by hydrogen bonding [Nishikido, 1990]. This was observed in MSU-X silicas [Bagshaw et al., 1995; Prouzet et al., 1999] and aluminas [Bagshaw and Pinnavaia, 1996]. The same holds for the present zirconium mesophase prepared with Tween surfactants.

CONCLUSIONS

The zirconium mesophase has been synthesized for the first time by using zirconium chloride and Tween surfactants in an aqueous medium. The surfactants should be removed not by calcination but by treatment with UV light and in-situ generated ozone because this mesophase has a thin inorganic wall. The UV/ozone-treated Tw-X–ZrO_2 (X=20, 40, 60 or 80) is found to have a wormhole structure by XRD and TEM analyses. This is in contrast to the result reported by Yang et al. [1998, 1999], although the synthesis was carried out under the same acidic conditions. It is worth noting that the mesoporous zirconia of this study is synthesized by using different kinds of PEO nonionic surfactant, Tween.

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