(54) Title: COMPOSITION AND METHOD FOR PRODUCING HEXAGONALLY-PACKED MESOPOROUS METAL OXIDE

(57) Abstract

The present invention relates to a composition and a method for producing hexagonally-packed mesoporous metal oxides wherein the metal oxide is selected from transition metals and lanthanide metals. The composition includes hexagonally packed metal oxide mesostructures that are resistant to pore collapse upon removal of surfactant and are thermally stable. The composition can include a surfactant complexed with the metal. Also described are methods for producing the hexagonally-packed mesoporous metal oxides.
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>Armenia</td>
<td>GB</td>
<td>United Kingdom</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>AT</td>
<td>Austria</td>
<td>GE</td>
<td>Georgia</td>
<td>MX</td>
<td>Mexico</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GN</td>
<td>Guinea</td>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GR</td>
<td>Greece</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>HU</td>
<td>Hungary</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>IE</td>
<td>Ireland</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>IT</td>
<td>Italy</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>JP</td>
<td>Japan</td>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>KE</td>
<td>Kenya</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KR</td>
<td>Republic of Korea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KZ</td>
<td>Kazakhstan</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>CI</td>
<td>Cote d'Ivoire</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>SG</td>
<td>Singapore</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LR</td>
<td>Liberia</td>
<td>SI</td>
<td>Slovenia</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LT</td>
<td>Lithuania</td>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>LU</td>
<td>Luxembourg</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>LV</td>
<td>Latvia</td>
<td>SZ</td>
<td>Swaziland</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MC</td>
<td>Monaco</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MD</td>
<td>Republic of Moldova</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>EE</td>
<td>Estonia</td>
<td>MG</td>
<td>Madagascar</td>
<td>TJ</td>
<td>Tajikistan</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>ML</td>
<td>Mali</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>MN</td>
<td>Mongolia</td>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>MR</td>
<td>Mauritania</td>
<td>UG</td>
<td>Uganda</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
<td></td>
<td></td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>UZ</td>
<td>Uzbekistan</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
</tbody>
</table>
COMPOSITION AND METHOD FOR PRODUCING HEXAGONALLY-PACKED
MESOPOROUS METAL OXIDE

Background of the Invention

Porous inorganic solids have found great utility as catalysts and separation media for industrial applications. The openness of the microstructure allows molecules access to the surface area of the materials that enhance their catalytic and sorption activity. The porous materials in use today can be sorted into several categories based on their microstructure, molecular sieves being one of these.

Molecular sieves are structurally defined materials with a pore size distribution that is typically very narrow because of the crystalline nature of the material's microstructure. Examples of molecular sieves are zeolites and mesoporous materials. Zeolites are generally aluminosilicate materials with pore sizes in the microporous range which is between two to twenty Angstroms.

Mesoporous materials, however, generally have larger pore sizes. Mesoporous materials have a pore size from about 10 to 500 Angstroms. Examples of conventional mesoporous solids include silicas and modified layered materials, but these are amorphous or 2-dimensional crystalline structures, with pores that are irregularly spaced and broadly distributed in size. Pore size has been controlled by intercalation of layered clays with a surfactant species, but the final products have typically retained the layered nature of the precursor material.

Porous transition metal oxides have been the subject of increasing interest as materials which can be utilized in partial oxidation, complete combustion, NOx decomposition, hydrodesulfurization, photocatalytic decomposition of organic compounds and solid acid catalysis. Most attempts, however, to prepare mesoporous
materials suitable for such purposes have typically led to lamellar phases where surfactant and metal oxide phases are layered.

Efforts to synthesize hexagonally-packed mesoporous oxides have focused on an inverse-micelle template mechanism. Inorganic precursors, pH and surfactant head groups have been adjusted to achieve optimal electrostatic charge balance between the organic and inorganic phases during the self assembly process. This led to the synthesis of silica-based mesoporous materials as disclosed in U.S. Patent No. 5,098,684. Efforts to extend this approach to non-silica or alumina-based systems have mostly led to formation of layered phases. The few hexagonally-packed mesostructures derived by such approaches, composed of tungsten, antimony, lead and iron oxides, were not found to be thermally stable upon surfactant removal or thermal treatment (Huo et al. Chem. Mater. 6:1176 (1994)). High surface areas and well-defined porosities for transition metal products could not be achieved in these systems upon surfactant removal in contrast to alumina- and silicate-based systems mentioned above.

One reported example of a transition metal-containing hexagonally packed mesoporous material has only a small percentage of titanium dioxide incorporated into a silica structure. (Tanev et al. Nature 368:321 (1994)). The method used to form the hexagonal mesoporous materials utilized a primary, rather than a quaternary ammonium ion surfactant as the templating reagent. The titanium-doped silicate-based hexagonal mesoporous materials were found to be more active in the catalytic oxidation of arenes than the conventional microporous titanium silicate zeolites.

Therefore, a need exists for a thermally stable mesoporous transition metal material and a method for forming mesoporous transition metal materials which overcome or minimize the above mentioned problems.
Summary of the Invention

The present invention relates to a composition and a method for producing stable hexagonally-packed metal oxide mesostructure (TMS1) wherein the metal oxide is selected from transition metal oxides and lanthanide metal oxides.

A method for producing a stable hexagonally-packed mesoporous metal oxide includes combining a transition metal oxide precursor or lanthanide metal oxide precursor and a surfactant, having an appropriate head group, under conditions which are suitable for causing the formation of a complex between the head group of the surfactant and the metal oxide precursor in the substantial absence of water. Water is then added to the complex and the reaction mixture is maintained at conditions suitable for micelle formation and hydrolysis of the oxide precursor. The hydrolysed complex is aged for a period of time at a temperature suitable for causing the formation of hexagonally-packed mesostructures. The surfactant, or organic portion of the surfactant, is removed from the metal oxide mesostructure, resulting in the stable mesoporous material. The metal oxide is selected from transition metal oxides and lanthanide metal oxides.

In a second embodiment of the method of the present invention, a stable hexagonally-packed mesoporous metal oxide is prepared by combining a transition metal oxide precursor or lanthanide metal oxide precursor, a surfactant having an appropriate head group under conditions suitable for causing the formation of a complex between the head group of the surfactant and the metal oxide precursor, an aqueous solvent and a chelating agent (such as a 2,4-diketone) added in an amount to decrease, without arresting, the rate of hydrolysis. The complex is then maintained under conditions suitable for controlled micelle formation and hydrolysis of the metal oxide precursor. The hydrolysed complex is aged for a period of time at a
temperature suitable for causing the formation of a hexagonally packed metal oxide mesostructure. The surfactant, or organic portion of the surfactant, is removed from the metal oxide mesostructure, resulting in the stable mesoporous material. The metal oxide is selected from transition metal oxides and lanthanide metal oxides.

This invention has the advantage, for example, of enabling the formation of hexagonally-packed mesoporous metal oxides that are stable. In contrast to available materials, hexagonally packed transition metal oxide or lanthanide metal oxide mesostructures prepared by the present method are stable, i.e. they substantially retain the hexagonal mesostructure upon removal of the surfactant, thereby presenting a hexagonally packed mesoporous structure with well-defined pore diameter and morphology.

Brief Description of the Figures

Figure 1 is XRD (powder X-ray diffraction) data of Ti-TMS1 obtained using a phosphate surfactant with a chain length of 14 carbons atoms.

Figure 2 illustrates the XRD (powder X-ray diffraction) patterns of Nb-TMS1 synthesized with tetradecylamine. The d-spacing for the (100) reflection appears at 31 Å, the secondary (110), (200), and (210) reflections appear between 4° and 7° 2θ, however the (110) and (200) peaks are not well resolved. Pattern (a) represents the result of surfactant removal by calcination. Pattern (b) represents the result of surfactant removal by washing with ethanol/H₂O/HNO₃ at 40°C and pH = 2.

Figure 3a is the N₂ adsorption-desorption isotherms for Nb-TMS1 synthesized with tetradecylamine after surfactant removal. The lack of hysteresis in the isotherms indicates the cylindrical nature of the pores.
Figure 3b depicts the pore size distribution of Nb-TMS1, illustrating the narrow pore opening range, centered at 27 Å. Figures 4A, 4B and 4C represent the micellar array of (C_{12}H_{25}NH_{2})Nb(OEt)_5, alkoxide and Nb-TMS1 respectively.

Figure 5 shows the XRD patterns of Ti-TMS-1 synthesized at pH=4 and 2:1 acetylacetone:metal ratio, with varying metal:surfactant ratios.

Figure 6 shows the XRD patterns of Ti-TMS-1 synthesized at pH=4 and 1:1 metal alkoxide:surfactant ratio, with varying acetylacetone:metal ratios.

Figure 7 shows the XRD patterns of Ti-TMS-1 synthesized at pH=7 and 1:1 metal alkoxide:surfactant ratio, and 1:1 acetylacetone:metal ratio, with varying C_{12} surfactant head groups.

**Detailed Description of the Invention**

The features and other details of the method of the invention will now be more particularly described with reference to the accompanying Figures and pointed out in the claims. It will be understood that particular embodiments of the invention are shown by way of illustration and not as limitations of the invention. The principle features of this invention can be employed in various embodiments without departing from the scope of the invention.

It is reported herein that hexagonally packed transition metal oxide molecular sieves can be synthesized by a ligand-to-metal surfactant interaction in which the propagating metal fragment is incorporated into the surfactant head group. A metal oxide precursor is chemically linked to one or more heteroatoms in the head group of a surfactant molecule. The resulting organometallic species is then subsequently hydrolyzed and
subjected to conditions which result in micelle formation, thereby resulting in the hexagonally-packed mesostructure. These hexagonally-packed mesostructures are stable enough so that the structure is substantially maintained after the surfactant is removed under conditions which break the chemical interaction between the metal and the head group heteroatom of the surfactant such that the surfactant is removed from the structure.

One embodiment of the present invention is a composition comprising a hexagonally-packed mesoporous metal oxide, wherein the metal oxide is selected from transition metals and lanthanide metals, in which a heteroatom on the head group of a surfactant is coordinated or complexed with the metal. A "hexagonally-packed mesoporous structure" is a structure with a regular hexagonal array of channels having a substantially uniform diameter or "pore" size ranging from about 10 Å to about 500 Å, preferably from about 20 Å to about 200 Å, more preferably from about 20 Å to about 50 Å.

A "transition metal", as used herein, is an element designated in the Periodic Table as belonging to Group IIIB (e.g. scandium and yttrium), Group IVB (e.g. titanium, zirconium and hafnium), Group VB (e.g. vanadium, niobium and tantalum), Group VIB (e.g. chromium, molybdenum and tungsten), Group VIIB (e.g. manganese, technetium and rhenium), Group VIIIB (iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium and platinum), Group IB (e.g. copper, gold and silver) and Group IIB (zinc, cadmium and mercury). A "lanthanide metal" is a metal belonging to the lanthanide series in the Periodic Table (e.g. lanthanide, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium). Preferred metals include titanium, niobium, cerium, yttrium, zirconium and tantalum.
A "transition metal oxide", as used herein, is a transition metal bonded to one or more oxygen atoms. A "lanthanide metal oxide", as used herein, is a lanthanide metal bonded to one or more oxygen atoms.

"Coordinated" or "complexed" with the metal refers to a strong ligand interaction between one or more atoms within the head group of the surfactant and the metal that is greater than typical electrostatic interactions, van der Waals interactions or hydrogen bonding. In one aspect, the strength of the interaction can be on the order of covalent bonding. The "head group" is the polar or hydrophilic functional group of the surfactant. The "tail" is the hydrophobic group of the surfactant.

Another embodiment of the present invention is a stable hexagonally-packed mesoporous metal oxide wherein the metal is selected from transition metals and lanthanide metals. As used herein, a "stable hexagonally-packed mesoporous metal oxide," wherein the metal is selected from transition metals and lanthanide metals, is one in which the metal oxide substantially maintains a hexagonal mesostructure following removal of the surfactant or tail group of the surfactant. The hexagonal mesostructure is maintained with a narrow range of pore diameter following removal of the surfactant or tail group of the surfactant (hereinafter collectively referred to as removal of the surfactant). Following removal of the surfactant, the stable hexagonally-packed mesoporous metal oxide wherein the metal is selected from transition metals and lanthanide metals of the present invention would have an accessible surface area of 50-1200 m²/g. A stable hexagonal mesostructure is also indicated by the substantial preservation of the hexagonal powder X-ray diffraction pattern (XRD) of metal oxide after removal of the surfactant compared with prior to removal. Typically, the stable hexagonal mesostructures of the present invention
would correspond to a narrow pore size distribution with at least 50 m²/g of B.E.T. (Brunauer-Emmett-Teller) surface area.

In one aspect, "stable" refers to thermal stability. As used herein, "thermally stable" means that the mesoporosity and B.E.T. surface area of the surfactant-free hexagonal mesoporous structures remain substantially unchanged at temperatures above about 50° C and below about 800° C, preferably below about 600° C. Preferably, the loss of accessible surface area of the mesostructure upon thermal treatment is less than 20%, more preferably less than 5%.

In another aspect, "stable" refers to the stable preservation of hexagonal mesostructure upon surfactant removal by calcination. Hexagonally packed mesostructures are resistant to calcination when heated in an oxidizing atmosphere below about 500° C for surfactant removal.

Optionally, the hexagonally-packed metal oxide mesostructures, wherein the metal oxide is selected from transition metals and lanthanide metals, of the present invention can additionally comprise one or more different inorganic oxides or metal salts. Suitable inorganic oxide dopants include oxides of transition metals, lanthanides, alkali metals (Group IA), alkaline earth metals (Group IIA), and main group metals (Group IIIA-VIIA). Preferably, the inorganic oxides are oxides of Y, V, Ti, Zr, Ir, Os, Rh, Pt, Pd, Au, Fe, R, Ru, Cu, Co, Hg, Tl, Ni, and/or Cr. Suitable metal salts include alkali metal salts, alkaline earth metal salts and transition metal salts. Preferred salts include alkali metal halides, such as KCl and NaCl. Such hexagonally-packed mesoporous metal oxides can be prepared by "doping" as is generally known in the art, for example, or including a corresponding inorganic precursor in the processes described herein. Suitable concentrations
of the inorganic oxide are from about .1 mole % to about 50 mole %, preferably from about 1 to about 10 mol %.

The preparation of hexagonally-packed mesoporous metal oxides involves first complexing a heteroatom with the metal of a metal oxide precursor before allowing substantial micelle formation and/or hydrolysis to occur. In contrast, previous methods of preparing a hexagonally-packed mesoporous transition metal oxide involve pre-formation of a micelle template around which the metal oxide assembles, drawn by electrostatic forces (Huo et al., Chem. Mater. 6:1176 (1994)). However, hexagonally-packed transition metal oxide mesostructures prepared by this method have not been stable, i.e. the mesostructure is not maintained after removal of the surfactant.

One embodiment of the present invention is a method of preparing a hexagonally-packed mesoporous metal oxide wherein the metal oxide is selected from transition metals and lanthanide metals. A transition metal oxide precursor or lanthanide metal oxide precursor and a surfactant are combined under conditions which cause the formation of a complex between a heteroatom in the head group of the surfactant and the metal of the metal oxide precursor in the substantial absence of water. The reactants can be contacted in the presence of a suitable organic solvent, such as in an alcoholic solvent (Example 2) or can be carried out neat (Example 4). The complex thus formed is subjected to conditions suitable for micelle formation and hydrolysis of the metal oxide precursor. This reaction product is then allowed to age for a period of time and at a temperature suitable for causing the formation of a hexagonally-packed metal oxide mesostructure.

Optionally, a metal salt is added to the mixture being aged in an amount sufficient to accelerate the formation of hexagonally-packed metal oxide mesostructure. Suitable
metal salts include Group IA metal salts (alkali metal salts), Group IIA metal salts, transition metal salts and lanthanide metal salts. Alkali halides (e.g., potassium chloride) are preferred. Typically, about 0.1-20.0 equivalents of metal salt are sufficient to cause an increase in the crystallization rate; about 0.5-2.0 equivalents is preferred.

Alternatively, the metal oxide precursor can be contacted with the surfactant in the presence of water. In this embodiment, prior to precursor addition, the surfactant and precursor are contacted in a quantity of water such that the surfactant concentration is above the critical micelle concentration, i.e. the concentration of surfactant below which micelles do not form. The "critical micelle concentration" (i.e., the concentration at which micelles form) varies dependent upon the surfactant and can be determined, for example, by applying varying amounts of the surfactant to a constant quantity of water and determining the concentration at which micelles do not form. In certain instances, it is advantageous to additionally add a chelating agent, such as a 2,4-diketone (e.g. acetylacetone) to the metal oxide precursor (preferably prior to contacting the precursor with surfactant and/or water) in order to prevent premature hydrolysis of the metal oxide precursor. It is preferable to use acetylacetone when using metal oxide precursors of yttrium, titanium and zirconium. Typically, about 0.1 to about 10 equivalents of acetylacetone to metal oxide precursor, preferably about one equivalent, are added to the reaction mixture.

A transition metal oxide precursor is a compound comprising a transition metal which as a result of a chemical reaction (such as hydrolysis and polycondensation) forms a transition metal oxide. Examples include transition metal alkoxides, transition metal salts,
transition metal hydroxides, or colloidal dispersions of transition metal oxides or transition metal hydroxides. Transition metal alkoxides are preferred.

A lanthanide metal oxide precursor is a compound comprising a lanthanide metal which as a result of a chemical reaction (such as hydrolysis and polycondensation) forms a lanthanide metal oxide. Examples include lanthanide metal alkoxides, lanthanide metal salts, lanthanide metal hydroxides, or colloidal dispersions of lanthanide metal oxides or lanthanide metal hydroxides. Lanthanide metal alkoxides are preferred.

A suitable surfactant is a straight chain hydrocarbon having a head group, wherein the head group is defined above. The straight chain hydrocarbon can have from about 8 to 24 carbon atoms, preferably from about 12 to 18 carbon atoms. The size of the micelles is determined, in part, by the size or length of the surfactants used. The length of the hydrocarbon tail of the surfactant can be used to vary the pore size of the hexagonally packed mesostructure.

Swelling agents can be added to the hydrophilic regions of the micelles to further increase the pore diameters. Examples of swelling agents include mesitylene, xylene, toluene and ethanol. In general, the swelling agent is hydrophobic and resides within the tail group regions of the inverse micelle upon addition to the surfactant solution.

Pore sizes can range from about 20 Å to about 200 Å, and preferably 20 Å to about 40 Å.

The materials of the present invention are characterized by the regularity of its large open pores in arrangement and size (pore size distribution within a single phase of, for example, ± 25%, usually ± 15% or less of the average pore size of that phase). The term "hexagonal" is intended to encompass materials that exhibit a hexagonal symmetry including significant observable
deviations, for example \( \pm 25\% \) random deviation from the repeat distance between adjacent channels.

Suitable head groups include phosphate, carboxylate, sulfate, amino and acetylacetonate. The stability of hexagonally-packed mesostructure formation can be dependent on the optimization of the head group of the surfactant and the precursor. That is, the surfactant head group is selected to form an optimal complex with the precursor (e.g., a strong ligand interaction). For example, titanium, cerium and zirconium containing metal oxide precursors (e.g. titanium isopropoxide, cerium isopropoxide and zirconium n-propoxide) formed stable hexagonally packed mesostructures when combined with surfactants having phosphate head groups. Stable hexagonally packed niobium and tantalum mesostructures were prepared with niobium and tantalum oxide precursors (e.g., niobium ethoxide and tantalum ethoxide) and neutral amine surfactants. Sulfate surfactants formed strong ligand interactions with yttrium oxide precursors, such as yttrium isopropanoxide. The optimal surfactant head groups for each metal can be determined by routine experimentation in which the method of preparing hexagonally packed metal oxide mesostructures is carried out in the presence of various surfactants having different head groups. Such an optimization is described in Example 7. Surfactant/metal oxide precursor ratios can vary from about 1:1 to about 1:9 and is preferably about 1:1, e.g., for the titanium oxide precursor (Example 6).

Conditions suitable for micelle formation and hydrolysis of the metal oxide precursor refer to adding sufficient water to the surfactant/metal oxide complex such that the concentration of surfactant is above the critical micelle concentration. Micelle formation is preferably carried out with cooling to temperatures of about \(-78^\circ C\) to about \(0^\circ C\), following which water is added and the mixture
is allowed to warm to room temperature to promote hydrolysis. Temperatures as high as about 50°C can be used.

The period of time suitable for causing the formation of hexagonally packed metal oxide mesostructures varies according to the metal oxide precursor and temperature selected. In general, aging lasts from about 1 minute to about 14 days, preferably from about one hour to about fourteen days, and more preferably about 3-7 days.

Suitable temperatures for aging can range between about 15°C to about 200°C. Optimal time periods can be determined from the XRD pattern through comparison of intensities and resolution of the peaks corresponding to the hexagonal structure. Time periods are chosen to maximize the distinctness of these peaks. For example, an XRD pattern for hexagonally packed titanium oxide mesostructure made with 0.5-1 mol equivalents of potassium dodecyl phosphate isolated after one day aging at room temperature had a diffraction pattern in which the (100) peak was broad and the smaller peaks were not clearly distinguished. The low-intensity (110), (200), and (210) peaks became more intense and distinct when the sample was aged for longer periods.

In general, materials aged at room temperature generally had broad humps at around 2°2θ in the XRD. When the aging temperature is increased to over 100°C, decomposition of the mesostructure occurs with the premature removal of surfactants in the case of Zr, Ce, and Ti oxides with phosphate surfactants. For Nb and Ta oxides with amino surfactants, aging temperatures below about 180°C, can be used without mesostructure decomposition. Optimal aging temperatures can be readily determined by one skilled in the art by carrying out the aging process at various temperatures and then examining the XRD peaks of the hexagonal pattern for sharpness, as described above.
Optimal aging temperatures and aging times for hexagonally-packed niobium oxide, yttrium oxide, zirconium oxide, titanium oxide and tantalum oxide mesostructures are given in the Examples.

The pH and ionic strength of the solution in which the hydrolysis, micelle formation and aging occur can vary over a wide range. However, the rate of hydrolysis, the rate of aging or polycondensation and the quality of the hexagonally-packed mesostructures, as determined by the intensity and resolution of the hexagonal XRD pattern, is affected by these parameters and can vary according to the metal oxide precursor. Generally, the pH used in the aging process can range from about 1-14, but is preferably between about 3-8. In the specific case of titanium oxide precursors, the preferred pH ranges between about 4-6. Preferred pHs for hexagonally-packed niobium oxide, yttrium oxide, zirconium oxide, and tantalum oxide mesostructures are given below in the Examples. One of ordinary skill in the art can determine optimal pHs and ionic strengths for other metal oxide precursors using the methods described herein, for example.

As set forth above, the invention relates to the formation of a strong ligand interaction or complex between the surfactant head group and the metal oxide precursor prior to the substantial formation of micelles, hydrolysis and polycondensation of the metal oxide. This favors the ligand assisted templating of hexagonal mesostructure formation instead of layered or amorphous phase formation. The chemical or ligand bond can be subsequently broken by suitable treatment to allow surfactant removal without significant disturbance of the mesostructure.

In a preferred embodiment, the surfactant is removed by chemical means. Typically, this is carried out by washing the hexagonally-packed mesostructure with a solution which is capable of breaking the coordination
between the metal and the head group of the surfactant without substantially disturbing the hexagonal metal oxide mesostructure. One example of a chemical means of removing the surfactant from the hexagonally-packed mesostructures is by washing with a suitable solvent under acidic or basic conditions. For example, the titanium oxide mesostructure of Example 1 can be washed with an alcohol solvent, such as ethanol, in the presence of a strong base, such as potassium hydroxide. The resulting B.E.T. surface area from a sample prepared from C$_{14}$H$_{29}$ phosphate was 420 m$^2$/g.

In another example of a chemical means of removing the surfactant, hexagonally-packed niobium oxide mesostructures prepared as described herein are washed with a strong acid, such as nitric acid, in a suitable solvent, such as ethanol. Evidence that the material had retained the hexagonal mesostructure was provided by the resulting B.E.T. surface area, which was 434 m$^2$/g. In addition, the N$_2$ adsorption-desorption isotherms of Nb-TMS1 (Figure 3a) presented no hysteresis, indicating the cylindrical nature of the pores. The pore size distribution of this material (Figure 3b) involved one narrow peak at 27 Å. Washing the surfactant containing niobium oxide mesostructure with ethanol produced material with a B.E.T. surface area of about 5 m$^2$/g, contrasting with recent results which showed that amine surfactants could be removed from samples of silica- and alumina-based mesoporous materials prepared using the inverse micelle assisted-crystallization procedure by stirring them in ethanol at room temperature (Tanev et al., Nature 267:865 (1995)). This result indicated that the interaction between the surfactant head group and the metal was significantly stronger in mesostructures prepared by the method of the present invention than the electrostatic interactions between the silicon or aluminum and the surfactant head group in mesostructures prepared by Tanev et al.
In another aspect, the surfactant can be removed by calcination. This process is carried out by heating the sample at a sufficient temperature and for a sufficient period of time to combust the surfactant. Suitable temperatures are up to about 600°C, preferably at about 200°C to about 500°C. Sufficient time periods vary from about 1 hour to about 24 hours, and are preferably from about 6 hours to about 10 hours. Hexagonally-packed titanium oxide mesoporous structures were substantially preserved in calcination at 550°C under air or oxygen. Some structural collapse occurred as illustrated by some broadening of the XRD pattern of the calcined sample as compared to the as synthesized sample which still retains the surfactants. This damage could be due to a light-off which occurs at about 170°C, possibly catalyzed by the titania, which has been found to be an effective catalyst in C-H bond oxidation processes (Neumann et al., J. Chem. Soc. Commun. 22:1685 (1993)). The B.E.T. surface area of calcined mesoporous TiO₂ was obtained by using N₂ adsorption and was found to be 150 m²/g. Similarly, calcination of synthesized niobium mesostructures at 500°C for five hours yielded a material with partial pore collapse and a surface area of 61 m²/g.

Calcining of hexagonally-packed titanium oxide mesostructures before extensive drying gave an extensive degree of structural collapse, most likely due to low hydrothermal stability. This was also evidenced by the fact that aging in the presence of water at temperatures in excess of 100°C led to degradation of the mesoporous structure and concomitant formation of amorphous material. Transmission Electron Micrographs (TEM) of the material showed dried Ti-TMSi with its hexagonal structure substantially intact after calcination. Similar structural stability has been noted for the zirconium, niobium and tantalum systems, but not the yttrium system, which
converted to a layered phase at 100°C. The XRD of calcined Ti-TMS1 shows a substantially broadened (100) peak with poorly defined (110), (200), and (210) peaks.

A hexagonally-packed niobium oxide mesostructure was prepared by the method of the present invention. A solution of niobium ethoxide (Nb(OEt)₄) (5.0 g) in isopropanol (10 ml) was treated with tetradecyl amine (3.4 g, 1 equivalent), resulting in a octahedral niobium amino ethoxy complex (Mehrotra et al., Inorg. Chim. Acta 16:237 (1976)). When this solution was further treated with water (20 ml), a rapid polymerization reaction ensued giving a white gelatinous precipitate. Aging this gel at 150°C for ten days yielded a white powder (Nb-TMS1) with the characteristic hexagonal X-ray powder diffraction pattern (XRD) shown in Figure 2, similar to those recorded for MCM-41. The TEM of Nb-TMS1 confirmed that a pure transition metal oxide structural analogue of hexagonally packed mesoporous MCM-41 was obtained.

The preparation and characterization of surfactant-free Nb-TMS1 is described in the application. Surfactant-free Nb-TMS1 has novel and useful properties. This material exhibits a high thermal and hydrothermal stability as indicated by nitrogen adsorption, revealing that this material has a stable mesoporosity and surface area to at least 400°C. These results indicated that Nb-TMS1 synthesized by this novel approach would be useful as a high surface area catalytic material with thermal stability and uniform pore sizes. As a transition metal oxide with variable oxidation states, Nb-TMS1 would also offer additional unique catalytic properties not possible in the conventional alumina- or silicate-based MCM-41 systems.

The mechanism of forming Nb-TMS1, C, (shown in Figure 4C) is depicted below:
The invention represents a novel approach to the synthesis of mesoporous materials in that the surfactant, C₁₂H₂₅NH₂, is chemically bonded to the metal atom in the precursor, Nb(OEt)₅, as organometallic precursor, (C₁₂H₂₅NH₂)Nb(OEt)₅, and possibly throughout the entire aging process. This mechanism contrasts to that proposed for the synthesis of MCM-41, where a ligand interaction between the tetraalkylammonium surfactant head group and the Si center is neither present nor possible. For the latter case, it has been proposed that the surfactant phase templates the assembly of the inorganic phase via either preformed micelles (Chen et al., Microporous Mater. 2:27 (1993)) or electrostatic charge matching between the silicate oligomers and the individual surfactant head groups (Huo et al. Nature 368:317 (1994); Monnier et al. Science 261: 1299 (1993); Huo et al. Chem. Mater. 6:1176 (1994)). In the synthesis of Nb-TMS1, C (Figure 4C), such a mechanism is not feasible since the surfactant, (C₁₂H₂₅NH₂)₂, is not soluble in water under the synthesis conditions applied. Employing the described ligand-assisted templating mechanism, the Nb-N bond present in the organometallic precursor, (C₁₂H₂₅NH₂)Nb(OEt)₅, is believed to remain intact during at least the initial phase of the synthesis. If the ammonium form of the surfactant was dominant, Nb-TMS1, C (Figure 4C), could be formed starting from the alkyl ammonium salt. At the neutral pH regions that favored Nb-TMS1, C (Figure 4C), formation, however only amorphous materials were produced with these alternate surfactants. Also, while the organic phase in samples MCM-41 prepared with amine surfactants at neutral pH can be removed by
stirring in ethanol for one hour, little if any surfactant is removed from Nb-TMS1 under these conditions. This suggests that Nb-N bonds may well be intact in the as-synthesized material.

The reaction scheme, I, above, represents the two possible synthesis pathways for Nb-TMS1, C (Figure 4C), under a ligand assisted templating mechanism. In pathway A, the organometallic precursor, \((\text{C}_{12}\text{H}_{25}\text{NH})_{3}\text{Nb(OEt)}_{5}\), self-assembles in ethanol prior to hydrolysis and this micellar array, A (Figure 4A), holds the Nb-containing head groups in place during subsequent hydrolysis to Nb-TMS1, C (Figure 4C). Although alcohol can disrupt micelle formation, this phenomenon is largely dependent on concentration of the surfactant and the dielectric constant of the medium. Due to the high concentrations of the niobium precursor used in the synthesis of Nb-TMS1 and the polar nature of ethanol, micelle formation is possible. Although the niobium head group is not hydrophilic, it is believed that because of ethoxy exchange with the free ethanol in the solvent, it would prefer to occupy regions of the solution rich in ethanol while the hydrophobic tail groups would tend to cluster together. Evidence for this is that organometallic ethoxide complexes are usually soluble in ethanol, while long chain hydrocarbons are not. In the second proposed pathway, B, the self-assembly occurs during hydrolysis and polycondensation of the alkoxide B, (Figure 4B) to Nb-TMS1, C (Figure 4C). The self-assembly of polymers containing hydrophobic and hydrophilic regions during chain growth has been noted before. Although the niobium head group is initially hydrophobic, the hydrolytic replacement of ethoxide groups with hydroxide and oxide linkages may have given rise to progressively more hydrophilic head group assembly in forming the final mesoporous structure depicted.

A hexagonally-packed titanium oxide mesostructure (Ti-TMS1 - Example 1) was prepared with titanium acetylacetonate tris-isopropoxide as a precursor and tetradecyl phosphate surfactant (10 wt.%) at pH 3-6 after five days aging at 80°C. The powder X-ray diffraction (XRD) pattern for isolated
synthesized Ti-TMS1 gives the expected (100) peak at a d spacing of 32 Å. No amorphous or layered phases were observed in this material, shown in Figure 1. TEM of the surfactant containing Ti-TMS1 showed the hexagonal array of stacked tubes of approximately 27 Å in pore diameter. The inner walls of this material were
about 5 Å thick, corresponding to what was expected on the
basis of the XRD data.

The B.E.T. surface area of calcined Ti-TMS1 was
obtained using N₂ adsorption and found to be 150 m²/g. When
the surfactant was removed by treatment with KOH in
ethanol/water at pH 9, the surface area was 420 m²/g. This
indicated that the mesostructure was preserved to a greater
degree than in those samples of Ti-TMS1 in which the
surfactant was removed by calcining. Also, the slightly
smaller surface area (420 m²/g) as compared to MCM-41 can
be attributed almost exclusively to the molecular weight
difference between SiO₂ and TiO₂.

The materials described herein can be utilized as
catalysts in partial oxidation reactions, combustion, NOₓ
decomposition, hydridesulfurization, photocatalytic
decomposition of organic compounds, absorbants and/or solid
acid catalysis, by methods generally known in the art. The
material of the invention can also be incorporated into a
matrix, such as a matrix derived from alumina, silica,
silica-alumina, titania, zirconia, clay or combination
thereof. Such a matrix can improve the crush strength of
the catalyst. In this embodiment, the matrix material is
added to the hexagonally-packed metal oxide mesostructure
in colloidal form and then extruded as a bead or pellet.
The content of the mesostructure within the matrix
generally ranges from about 1 to about 90 weight percent
and more particularly from about 2 to about 80 weight
percent.

The invention will now be further and specifically
described by the following examples. All parts and
percentages are by weight unless otherwise stated.

Example 1: Ti-TMS1 Preparation by the Aqueous Route
Tetradecyl phosphate (5.20 g, 17.6 mmol) was dissolved
in 25 ml of water with KOH (0.49 g, 17.6 mmol) and the pH
adjusted to 5.0 with 12.5 M HCl. In a separate beaker, titanium isopropoxide (5.0 g, 17.6 mmol) was treated with acetylacetone (0.9 mL, 17.6 mmol). The solution immediately turned yellow and heat was liberated. This solution was cooled and then added to the surfactant solution with vigorous stirring. The resultant thick yellow meringue was then aged at ambient temperature for two hours and then at 80°C for five days. The resulting fawn powder was collected by filtration, washed with three 100 ml portions of water, and subsequently dried in an oven at 120°C overnight. This product was calcined at 300°C in air for twelve hours to remove the surfactant. When calcination was conducted in a pure oxygen atmosphere, a light-off occurs at about 170°C leading to substantial pore collapse.

The above experiment was repeated except that the surfactant was removed from the product by reflux in EtOH/H₂O at pH 12 for 24 h. Washing the product with water, ethanol, and acetone gives Ti-TMS1 with surface areas in excess of 420 m²/g.

Figure 1 is XRD (powder X-ray diffraction) data of Ti-TMS1 with a first d-spacing of 32 Å, obtained using a phosphate surfactant with a chain length of 14 carbon atoms.

TEM's of Ti-TMS1 showed the hexagonal array of stacked tubes of approximately 27 Å in pore diameter. The inner walls of this material are approximately 5 Å thick, corresponding to what is expected on the basis of the XRD data.

Example 2: Ti-TMS1 Preparation by the Non-aqueous Route

Titanium isopropoxide (5.0 g, 17.6 mmol) and tetradeacyl phosphate (5.20 g, 17.6 mmol) were mixed with evolution of heat. After 1 h of stirring at room temperature, methanol (10 ml) was added and the resulting
solution was cooled to -78°C. Dilute hydrochloric acid (pH 5, 20 ml) was added dropwise to this suspension. The solution was warmed gradually to room temperature and left at ambient temperature for two hours. After addition of 1.0 g KCl, the solution was heated to 80°C for five days. The product was similar to that obtained in Example 1.

Example 3: Zr-TMS1 and Ce-TMS1 Preparation

Examples 1 and 2 were repeated, except zirconium n-propoxide or cerium isopropoxide were used as the precursor in place of titanium isopropoxide and calcination was carried out at 400°C in pure oxygen for ten hours.

Example 4: Nb-TMS1 and Ta-TMS1 Preparations

Niobium ethoxide (5.0 g, 15.7 mmol) was warmed with tetrade cylamine (3.4 g, 15.7 mmol) until a homogeneous yellow solution was obtained (~5 min, 50°C). To this solution was added 1 g KCl in 25 ml water with the immediate formation of a precipitate. The heavy solid was broken up with a spatula. The solid and supernatant were kept at room temperature for 2 h prior to heating the mixture at 95°C for five days. The product was collected by suction filtration and washed with three 100 ml portions of water. The solid was then dried at 120°C for 1 day and calcined in oxygen at 500°C for 5 h to give stable Nb-TMS1 with a B.E.T. surface area of 61 m²/g.

The experiment was again repeated, except surfactant was removed from the product by refluxing the solid in a mixture of 3:1 EtOH:H₂O ratio and nitric acid at pH below 1 for 24 h. The Nb-TMS1 obtained after washing with water, ethanol and acetone had a surface area in excess of 434 m²/g.

This experiment was repeated except that Ta(OEt)₅ was used in place of Nb(OEt)₅, resulting in stable Ta-TMS1. For a sample of Ta-TMS1 made with hexadecylamine aged at 150°C,
treated for 3 days and then treated with HNO₃, the surface area was 380 m²/gm.

Fig. 2, pattern a, is an XRD (powder X-ray diffraction) pattern of Nb-TMS1 synthesized with tetradecylamine. This data was recorded on a Siemens D-5000 diffractometer using CuKα radiation and a scintillation detector at 2.2 kW. The d-spacing for the (100) reflection appears at 31 Å, which is slightly smaller than the approximate value of 35 Å observed for as-synthesized MCM-41 made with tetradecyltrimethylammonium bromide, possibly reflecting the greater degree of extension of the trimethylammonium head group over the amine head group for the same surfactant chain length. The secondary (110), (200), and (210) reflections appear between 4° and 7° 2θ as expected, however the (110) and (200) peaks are not well resolved. This effect was observed before in samples of MCM-41 and Ti-doped MCM-41, and has been attributed to the small particle size and/or the regions of local disorder where the nanometer-sized tubes are not stacked in a perfectly hexagonal array.

Fig. 2, pattern b, is an XRD pattern of the same sample of Nb-TMS1 after ethanol/HNO₃ washes, which demonstrates that although the peaks are not as intense, the overall hexagonal structure was maintained after successful surfactant removal.

High resolution TEM micrographs of Nb-TMS1 synthesized using tetradecylamine were obtained with a JEOL 200 CX transmission electron microscope operated at 200 kV. Samples were prepared by sonication in isopropanol and suspension on carbon-coated copper grids. The pores were hexagonally packed, with an opening of approximately 27 Å and wall thickness of approximately 8 Å. The sum of these numbers agrees well with the value of 35 Å calculated for the hexagonal repeat distance, a₀ (a₀ = 2d_{100}/3^{1/2}), from XRD.
Fig. 3a is the \( \text{N}_2 \) adsorption-desorption isotherms for Nb-TMS1 synthesized with tetradecylamine and washed three times with ethanol/HNO\(_3\) at 40\(^\circ\)C. This data was obtained on a Micromeritics ASAP 2000 Sorption Analyzer using standard procedures. The isotherms display the sharp incline at values of P/P\(_0\) in the 0.3 to 0.5 range which is typical of the mesoporous materials produced with similar surfactant chain length. The absence of hysteresis also supports the cylindrical nature of the mesopores.

Fig. 3b depicts the pore size distribution of the same Nb-TMS1 sample, illustrating the narrow pore opening range, centered at 27 Å.

Example 5: Y-TMS1 Preparation by the Aqueous Route

Yttrium isopropoxide (5.0 g, 18.8 mmol) was dissolved in isopropanol (10 mL) with acetylacetone (1.93 ml, 18.8 mmol). The resulting solution was added to an acidic solution (pH = 4.5, HCl) of sodium n-tetradecyl sulfate (5.94 g, 18.8 mmol). The resulting mixture was heated overnight at 70\(^\circ\)C, collected by filtration and washed with three 50 ml portions of water. The product was dried in the open at ambient temperature to afford the desired Y-TMS1 with a first d-spacing of approximately 30 Å. The material was not stable at calcination temperatures greater than 200\(^\circ\)C.

Example 6: Aqueous Preparation Optimization Studies

Synthesis Optimization:

A series of 120 experiments were conducted to determine the optimal pH, molar ratio of surfactant, and molar ratio of acetylacetone in the synthesis of Ti-TMS1. The pH was varied in integer steps from 2-6, the acetylacetone-to-Ti ratio was varied from 0-3 in one integer steps, and the surfactant-to-Ti ratio was studied
at levels of 1:9, 1:6, 1:4, 1:3, 1:2, and 1:1. In all cases, one parameter was changed while the other two were held constant. The aging temperature and time were held constant at 80°C and five days, respectively. The weight percent of surfactant used was 7-10 % depending on the pH. This slight variation was necessary because the surfactant is less soluble at lower pH and higher ionic strength. In the appropriate weight percent and pH ranges, liquid crystal micelle formation for phosphates of chain length greater than 10 carbon atoms is favored (Cooper J. Am. Oil Chem. Soc. 40:642 (1960)). The quality of the materials was assessed by XRD which elucidates the presence and crystallinity of the hexagonal mesoporous phase in the synthesized materials. The parameters which seemed most critical were the acetylacetone concentration and the surfactant-to-Ti ratio. The effect of the pH was not dramatic in the precursor compositions which favor the formation of mesoporous structures.

**Surfactant-to-Ti Ratio Studies:**

The optimum surfactant-to-Ti ratio under all conditions examined was 1:1. Figure 5 shows the XRD patterns obtained for samples synthesized with Ti-to-surfactant ratios of 1:1, 3:1 and 9:1, respectively. Hexagonal structures with poorly defined XRD patterns were obtained for Ti-to-surfactant ratios of 2:1 - 4:1, while the materials were largely amorphous at 6:1. At 9:1, the surfactant effect was so small that only anatase was observed in all pH and acetylacetone concentrations.

**Acetylacetone-to-Ti Ratio Studies:**

The optimal molar ratio of acetylacetone to Ti was established at 1:1 as shown in Figure 6. In the absence of acetylacetone only amorphous materials or anatase were formed in all surfactant-to-Ti ratios and pH ranges. With
one equivalent of acetylacetone, the results were best at pH of 4-6, while at two equivalents the results were best at pH of 2-3, and the time it took for precipitation of the product increased from < 5 minutes to over 1 day. Lower pH was required to complete the hydrolysis when two equivalents of acetylacetone per mol Ti are used. Since the phosphate surfactant was not soluble at pH of less than 3, a higher pH was used with only 1 equivalent of acetylacetone. At three equivalents of acetylacetone, precipitation did not occur.

**pH Studies:**

The alteration of the pH had little effect on the system in acetylacetone and surfactant ratio domains where Ti-TMS1 formation was preferred. The main effect noted was acceleration or deceleration of the hydrolysis process and the requirement of further aging. At very low pH however, there was a tapering off of the product crystallinity. The experiments showed that the best conditions for Ti-TMS1 synthesis was a molar ratio of surfactant-to-Ti of 1:1, a molar ratio of acetylacetone-to-Ti of 1:1, and a pH of 4-6.

**Effect of Ionic Medium:**

It was determined that the addition of potassium chloride to the aging solution greatly accelerated crystallization. In the absence of any KCl, using the diprotic form of the surfactant (pH ~ 2.0 at 10 wt. % in water) only poorly crystalline materials were formed. Addition of one equivalent of KCl to this same mixture gives an XRD pattern similar to that obtained when using the potassium salt of the surfactant at pH 2, where the pH of the mixture was lowered by addition of HCl. Use of sulfuric acid or nitric acid leads to less crystalline products in general. The alkali halide induced crystallization rate enhancement has been noted previously
Example 7:  Surfactant Head Group Studies

In order to determine the ideal surfactant head group for the synthesis of Ti-TMS1 and related materials, a series of studies were conducted using C₄₄ hydrocarbons functionalized at the terminal position with trimethylammonium, sulfate, carboxylate, phosphate, amine, and acetylacetonate. Two general approaches were utilized. The first was to dissolve the mono-potassium salt of the anionic surfactant or the bromide salt of tetradecyl trimethylammonium bromide in water at a concentration above the critical micelle concentration (cmc) for that particular system followed by adjustment of the pH and addition of the Ti alkoxide acetylacetonate precursor (the aqueous route). The route was not applicable to the amine and acetylacetonate surfactants because of the very low pKₐ of the deprotonated form. The second approach involved first mixing the protic form of the anionic or neutral surfactant in ethanol with the Ti alkoxide acetylacetonate precursor (note: although acetoacetonate was not added normally in the non-aqueous approach, it was added in this example for comparison) followed by hydrolysis with water of a preadjusted pH from -78° to room temperature and subsequent aging. This approach was not used for tetradecyl ammonium bromide since it does not have a conjugate acid. Metal alkoxides react quickly with a wide variety of donor ligands. Below is a depiction demonstrating that the head group is chemically bonded to the Ti-alkoxide fragment.
Phosphate

Sulfate

Carboxylate

Acetylacetonate
In general the strength of the resulting metal-ligand interaction decreases according to the trend: acetylactonate > carboxylate > phosphate > sulfate. Amino ligands are difficult to place on this scale because they can form amino, amido, and imido complexes, the stability of which is largely dependent on the metal center and ancillary ligands. In all cases, the surfactant-to-Ti ratio was held at 1:1. The crystallinity of the materials were characterized by XRD, as shown in Figure 7.

Systems involving tetradecyl trimethyl ammonium bromide or sodium sulfate gave no mesoporous materials at pH ranging from 2 - 9 using both the room temperature and low temperature routes. The room temperature carboxylate system gave anatase at basic pH and could not be extended to acidic pH because the surfactant was not very soluble under those conditions. Using the low temperature route, however, low-crystallinity hexagonal materials were isolated at room temperature from pH 4 - 7. Further aging at 80°C led to phase separation and isolation of amorphous materials.

The acetylacetonate-functionalized surfactant (3-tetradecyl-2,5-pentanedione) worked the best in the series studied using the low temperature route, giving materials with broadened hexagonal patterns at room temperature. Further heating led to leaching away of the insoluble surfactant as a separate phase on top of the water layer. Since neither the carboxylate nor acetylacetonate surfactants are soluble in water to any degree, the equilibrium between the aqueous form and the unsolvated form of the surfactant lies heavily in favor of the latter, drawing the surfactant out of the system into a separate phase on the surface of the supernatant. In accordance with the low solubility of the surfactant and LeChatelier's principle, the organic is leached out of the biphasic liquid crystal micelles.
Potassium hydrogen tetradecl phosphatc works almost as well as tetradecl acetylacetonc in the low-temperature preparation, but vastly surpasses it during the aging process. While acetylacetonc is a much better ligand to Ti than phosphate (Johansson, Coord. Chem. Rev. 12:241 (1974)), the fact that the phosphate surfactant is soluble at pH 2-12 makes it possible to age these materials without phase separation induced surfactant loss from the liquid crystal phase. The materials produced by the low temperature route are identical to those obtained using the room temperature aqueous surfactant route as long as KCl is added to the mixture after warming to room temperature. The quality of the materials obtained using the low temperature route without any further aging follow the trend of the head group's donor abilities listed above, i.e. acetylacetonate > carboxylate > phosphate. Further aging, however, favors the phosphate system, presumably because of solubility of the free surfactant in the supernatant.

The amine surfactant works extremely well for the low-temperature synthesis of Nb-TMS1 and Ta-TMS1 at neutral pH using M(OEt)₆ (M= Nb, Ta) as a precursor. However, it leads only to amorphous materials in the case of titanium.

In summary, the preferred synthesis conditions for Ti-TMS1 involve either: a) the prior addition of tetradecl phosphatc to titanium acetylacetonate tris-isopropoxide, followed by hydrolysis from -78°C to 80°C at pH 4-6 at a 1:1 surfactant-to-Ti ratio in the presence of 1 equivalent of KCl, or b) the addition of titanium acetylacetonate tris-isopropoxide to a 10 weight % solution of the mono-potassium salt of the surfactant at pH 4-6 followed by aging at 80°C for several days.
Example 8: Aging Studies

In a series of experiments, it was found that the Ti-TMS1 materials isolated at room temperature generally had broad humps at around 2° 2θ in the XRD. This is also observed in the synthesis of MCM-41 (Chen et al., Micropor. Mater. 2:27 (1993)) and has been attributed to low hexagonal order of the nano-tubes. When the temperature was increased over 100°C, transformation of the structure into first amorphous material and finally anatase was observed. Similar transformation of hexagonal mesoporous structures has been noted for MCM-41, however it occurs at temperatures in excess of 150°C, leading to zeolitic phases whereby the surfactant is believed to have curled up inside a microporous cavity (Beck et al., Chem. Mater. 6:1816 (1994)).

Example 9: Doping with Another Alkoxide

Nb(OEt)_5 (4.5 g, 0.0141 mol) was warmed to 60°C with octadecylamine (4.22 g, 0.0157 mol) and vanadium oxide isopropanoxide (0.380 g, 0.0016 mol) for ten minutes. The resulting yellow oil was cooled to ambient temperature and then water (25 ml) was added with stirring, causing the immediate precipitation of an off-white mass. This mixture was left at ambient temperature overnight and then aged at 80°C for 1 day and 150°C for five days. The resulting beige solid was collected by filtration and washed with two fifty ml portions each of water, acetone, and ether to give a sample of 10 mol% V_2O_5-doped Nb-TMS1 with a (100) peak at a XRD d-spacing of 38 Å. The surfactant was removed as described in previous examples.

Example 10: Doping with Metal Salts

Nb(OEt)_5 (4.5 g, 0.0141 mol) was warmed to 60°C with octadecylamine (4.22 g, 0.0157 mol) for ten minutes and then cooled to ambient temperature. To this oil was added
a solution of AuCl₃ (0.120 g, 0.0016 mol) in water (25 ml), causing the immediate precipitation of a white solid. This mixture was left overnight at ambient temperature and then aged at 80°C for 5 days to give a deep maroon solid which was collected by filtration and washed with two fifty ml portions each of water, acetone, and ether. The resulting 10% Au₂O₃-doped Nb-TMS1 displayed the d-spacing for the (100) peak in the XRD at 38 Å. The surfactant was removed as described in other examples.

Example 11: Swelling Agents

Nb(OEt)₅ (5.0 g, 0.0157 mol) was warmed to 60°C with octadecylamine (4.22 g, 0.0157 mol) and mesitylene (3.0 g, 0.0250 mol) for ten minutes. The resulting solution was then cooled to ambient temperature and water (25 ml) was added with stirring. At this point a white solid mass separated from the solution. The mixture was left overnight at ambient temperature and then aged with addition of 1.0 g KC1 for 1 day at 80°C followed by five days at 150°C. The resulting solid was collected by filtration and washed with two fifty ml portions each of water, acetone, and ether. The material thus synthesized has a (100) peak at a d-spacing of 55 Å as recorded by XRD. The surfactant was removed as described in previous examples. Without the addition of mesitylene swelling agent, the d-spacing of the product would have been 38 Å.

Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the following claims.
What is claimed is:

1. A molecular sieve comprising a hexagonally-packed mesoporous metal oxide wherein the metal of the metal oxide is selected from the group consisting of transition metals and lanthanide metals.

2. The molecular sieve of Claim 1 wherein the hexagonally packed mesoporous metal oxide is stable upon surfactant removal.

3. The molecular sieve of Claim 1 wherein the hexagonally packed mesoporous metal oxide is resistant to pore collapse upon calcination below about 600° C.

4. The molecular sieve of Claim 1 wherein the hexagonally packed mesoporous metal oxide has a narrow pore size distribution and a surface area of at least about 50 m²/g.

5. The molecular sieve of Claim 4 wherein the pore size distribution and surface area is substantially maintained upon heating the molecular sieve at temperatures below about 600° C.

6. The molecular sieve of Claim 2 wherein the metal of the metal oxide is a transition metal or lanthanide metal selected from the group consisting of niobium, titanium, zirconium, cerium, tantalum and yttrium.
7. The molecular sieve of Claim 2 wherein the hexagonally-packed mesoporous metal oxide has pores having an average diameter in a range of between about 20 to about 200 Å.

8. The molecular sieve of Claim 2 additionally comprising one or more inorganic oxide dopants.

9. The molecular sieve of Claim 8 wherein the inorganic oxide dopant is a metal alkoxide or metal salt wherein the metal is selected from the group consisting of Y, V, Ti, Zr, Ir, Os, Rh, Pt, Pd, Au, Fe, Re, Ru, Cu, Co, Hg, Tl, Ni, Cr.

10. The molecular sieve of Claim 9 wherein the inorganic dopant is present at a concentration from about .1 mole% to about 50 mole% of the composition.

11. The molecular sieve of Claim 1 further comprising a matrix.

12. A method of producing a hexagonally-packed metal oxide mesostructure comprising the steps of:
   a) combining a transition metal oxide precursor, or lanthanide metal oxide precursor and a surfactant having a head group, under conditions suitable for the formation of a complex between the head group of the surfactant and the metal oxide precursor;
   b) subjecting the product of step (a) to conditions suitable for micelle formation and hydrolysis of the metal oxide precursor; and
c) aging the product of step b) for a period of time and at a temperature suitable for causing the formation of a hexagonally-packed metal oxide mesostructure.

5 13. The method of Claim 12 wherein the transition metal oxide precursor or the lanthanide metal oxide precursor is a transition metal alkoxide or a lanthanide metal alkoxide.

14. The method of Claim 13 wherein a sufficient quantity of a metal salt is added to the product of step b) to accelerate the formation of the hexagonally-packed metal oxide mesostructure.

15. The method of Claim 14 wherein about 0.1-20.0 equivalents of an alkali metal halide are added to the product of step b) in step c).

16. The method of Claim 13 wherein the transition metal alkoxide or the lanthanide metal alkoxide, and the surfactant, are combined in step (a) in the substantial absence of water.

20 17. The method of Claim 16 wherein the product of step (b) is aged in step (c) for about 1 minute to about 14 days and the temperature is maintained at a temperature from about 15° C to about 200° C.

18. The method of Claim 13 wherein the transition metal alkoxide is titanium isopropoxide, zirconium n-propoxide or cerium isopropoxide and the surfactant has a phosphate head group.
19. The method of Claim 13 wherein the transition metal alkoxide is niobium ethoxide or tantalum ethoxide and the surfactant has a neutral amine head group.

20. The method of Claim 13 wherein the metal alkoxide is yttrium isopropoxide and the surfactant has a sulfate head group.

21. The method of Claim 12 further comprising:
   a) removing the surfactant from the product of step c) to produce a hexagonally-packed metal oxide mesostructure.

22. The method of Claim 21 wherein the surfactant is removed by washing.

23. The method of Claim 21 wherein the surfactant is removed by calcination.

24. The method of Claim 23 wherein the surfactant is removed by calcination at a temperature below about 600° C in an oxidizing atmosphere.

25. The method of Claim 12 wherein a swelling agent is added to step (a).

26. The method of Claim 25 wherein the swelling agent is selected from the group consisting of mesitylene, xylene, toluene and ethanol.

27. A method of producing a hexagonally-packed metal oxide mesostructure comprising the steps of:
   a) combining a transition metal oxide precursor, or lanthanide metal oxide precursor and a chelating agent;
b) combining the product of step (a) with a surfactant and water under conditions suitable for the formation of a complex between the head group of the surfactant and the metal oxide precursor, micelle formation and hydrolysis of the metal oxide precursor; and

c) aging the product of step b) for a period of time and at a temperature suitable for causing the formation of a hexagonally-packed metal oxide mesostructure.

28. The method of Claim 27 wherein the chelating agent is a 2,4-diketone.

29. The method of Claim 28 wherein the chelating agent is acetylacetone.

30. The method of Claim 29 wherein the transition metal oxide precursor or the lanthanide metal oxide precursor is a transition metal alkoxide or a lanthanide metal alkoxide, thereby forming a transition metal alkoxide acetylacetonate or a lanthanide metal alkoxide acetylacetonate in step (a).

31. The method of Claim 33 wherein a sufficient quantity of a metal salt is added to the product of step b) to accelerate the formation of the hexagonally packed metal oxide mesostructure.

32. The method of Claim 34 wherein about 0.1-20.0 equivalents of an alkali metal halide is added to the product of step b) in step c).
33. The method of Claim 30 further comprising:
   a) removing the surfactant from the product of step 
   c) to yield a hexagonally-packed mesoporous metal 
   oxide.

5 34. The method of Claim 33 wherein the surfactant is 
removed by washing.

35. The method of Claim 33 wherein the transition metal 
alkoxide acetylacetonate or the lanthanide metal 
alkoxide acetylacetonate are added in step (b) to an 
aqueous solution of surfactant at a surfactant 
concentration above the critical micelle 
concentration.

36. The method of Claim 33 wherein the product of step b) 
is aged for about 1 minute to about 14 days and the 
temperature is maintained at a temperature from about 
15° C to about 200° C.

37. The method of Claim 27 wherein the transition metal 
alkoxide is titanium tris-isopropoxide 
acetylacetonate, zirconium n-propoxide acetylacetonate 
or cerium isopropoxide acetylacetonate and the 
surfactant has a phosphate head group.

38. The method of Claim 37 wherein the metal alkoxide is 
yttrium isopropoxide acetylacetonate and the 
surfactant has a sulfate head group.

25 39. The method of Claim 37 wherein the surfactant is 
removed by calcination.
40. The method of Claim 39 wherein the surfactant is removed by calcination at a temperature below about 600° C in an oxidizing atmosphere.

41. The method of Claim 27 wherein a swelling agent is added to step (a).

42. The method of Claim 41 wherein the swelling agent is selected from the group consisting of mesitylene, xylene, toluene and ethanol.

43. The product produced by the process of Claim 12.

44. The product produced by the process of Claim 16.

45. The product produced by the process of Claim 18.

46. The product produced by the process of Claim 19.

47. The product produced by the process of Claim 20.

48. The product produced by the process of Claim 21.

49. The product produced by the process of Claim 27.

50. The product produced by the process of Claim 29.

51. The product produced by the process of Claim 33.

52. The product produced by the process of Claim 35.

53. The product produced by the process of Claim 36.

54. The product produced by the process of Claim 37.
FIGURE 5
1:1 M: Surfactant, pH = 4

FIGURE 6
C_{14} Chain Length, 24h, RT, pH=7 (3-9 Studied)

**FIGURE 7**
INTERNATIONAL SEARCH REPORT

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B C01G C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DAVID M. ANTONELLI &amp; AL.: &quot;Synthesis of hexagonally packed mesoporous TiO2 by a modified sol-gel method&quot; see the whole document ---</td>
<td></td>
</tr>
<tr>
<td>P,X</td>
<td>CHEMISTRY OF MATERIALS, no. 8, April 1996, WASHINGTON US, XP000576967</td>
<td>1-7, 12, 13, 16, 17, 19, 21, 22, 43, 44, 46, 48</td>
</tr>
<tr>
<td></td>
<td>DAVID M. ANTONELLI &amp; AL.: &quot;Synthesis and characterization of hexagonally packed mesoporous tantalum oxide molecular sieves.&quot; see the whole document ---</td>
<td>/-/-</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

Date of the actual completion of the international search

20 August 1996

Date of mailing of the international search report

26.08.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epos ni, Fax (+31-70) 340-3016

Authorized officer

Rigondaud, B
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P,X</td>
<td>ANGEWANDE CHEMIE INTERNATIONAL EDITION., vol. 35, no. 4, 1 March 1996, WEINHEIM DE, pages 426-430, XP000576116</td>
<td>1-7, 12, 13, 16, 17, 19, 21, 22, 43, 44, 46, 48</td>
</tr>
<tr>
<td>X</td>
<td>NATURE, vol. 368, 24 March 1994, LONDON GB, pages 317-321, XP000573990</td>
<td>1</td>
</tr>
<tr>
<td>X</td>
<td>CHEMISTRY OF MATERIALS, vol. 6, 1994, WASHINGTON US, pages 1176-1191, XP000573966</td>
<td>1</td>
</tr>
<tr>
<td>P,X</td>
<td>CHEMISTRY OF MATERIALS, vol. 7, no. 8, August 1995, WASHINGTON US, pages 1429-1430, XP000577423</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>HIGH TECH MATERIALS ALERT, vol. 10, no. 11, November 1993, ENGLEWOOD US, page 2 XP000406689</td>
<td>1</td>
</tr>
</tbody>
</table>

See figures 1, 2

See the whole document

"Generalized synthesis of periodic surfactant/inorganic composite materials"

"Organisation of organic molecules with inorganic molecular species into nanocomposite biphase arrays"

"Non silica-based mesostructured materials. 1. Synthesis of vanadium oxide-based materials"

"Engineer molecular sieves"