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RECOVERY OF ORGANIC TEMPLATES FROM POROUS MATERIALS USING SUPERCRITICAL FLUID EXTRACTION

FIELD OF INVENTION

The present invention relates to an improved method for the synthesis of porous inorganic materials widely used as catalysts, adsorbents, ion-exchangers, and separation media. Particularly, this invention relates to the application of supercritical fluid extraction as a fast, environmentally safe, and non-destructive method to recover organic templates efficiently from the pores of such freshly synthesized porous materials. More particularly, this invention proves suitable for recovering and recycling the expensive surfactant templates from freshly synthesized M41S mesoporous materials.

BACKGROUND OF THE INVENTION

The synthetic porous inorganic materials that are related to the present invention are characterized by substantially open microstructures. These porous inorganic solids, such as zeolites, are widely used as catalysts, adsorbents, ion-exchangers, and separation media for industrial applications. The starting synthesis mixtures of these porous materials contain a substantial amount of certain organic compounds as templating agents for pore structures. Pores are available only after the templates have been removed from the freshly synthesized samples. However, these organic templates are expensive and represent a major fraction of the overall production cost of such porous materials. As most of these porous materials are used in large quantities in industries, it is therefore of great



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economical value to find a fast, environmentally safe, and non-destructive method to recover and recycle these organic templates from the freshly synthesized porous materials in order to substantially reduce the production cost of these porous materials and to make these newly-developed porous materials more viable for commercial processes.

Prior to the advent of the present invention, the most common method to effectively remove these organic cationic templates from the pores of the synthetic material is by subjecting the freshly synthesized porous material to high temperature in air or in a controlled oxygen-containing atmosphere to slowly burn off the organic templates from the pores. In the art of the synthesis of molecular sieve or porous materials, this step of high temperature treatment is commonly referred to as calcination. However, high temperature calcination basically destroys or oxidizes the organic templates to CO_2 , H_2O , and some smaller toxic molecules. Alternatively, aqueous ion-exchange techniques could be used to remove the organic cationic templates from the pores; unfortunately, they are proven ineffective for removing the organic templates from layered and other porous materials. Also, U.S. Pat. 5,143,879 teaches that a liquid phase extraction method, which employs polar organic solvents and certain cationic donors, could be applied to extract these organic templates. However, due to the nature of liquid phase properties, the practical uses of this liquid phase extraction prove to be greatly limited due to its shortcomings. For example, U.S. Pat. 5,143,879 discloses that the liquid phase extraction requires hours or even days of operation, large volume of solvent consumption, and additional steps or procedures to condense the extracts or to separate the templates from the solvents and cationic donors.

Supercritical fluid extraction (SFE) is able to overcome the above shortcomings and has been recognized as an important alternative to extractions using liquid solvents [see, for example, S. B. Hawthorne, "Analytical-scale supercritical fluid extraction,"

Analytical Chemistry, 62 (1990) 633A]. Supercritical fluid is a compressed gas above its critical temperature and pressure. Supercritical fluids exhibit significant solvent strength or solvating power when they are compressed to liquid-like densities as molecular interactions are increased by shorter distances between molecules. By operating in the critical region, the pressure and temperature can be used to regulate density which in turn controls the solvent power of a supercritical fluid. In addition to its unique solubility characteristics, a supercritical fluid possesses certain other physicochemical properties that add to its attractiveness. For example, even though it possesses a liquid-like density over much of the range of industrial interest, it exhibits gas-like transport properties of diffusivity and viscosity [see, for example, Schneider et al, "Extraction with Supercritical Fluid Gases", p. 165, Verlag Chemie, 1980]. In fact, the diffusivity of a supercritical fluid is higher than that of a liquid by a factor of several hundreds. This means that mass transfer in a supercritical fluid is faster than a liquid by the same factor. The viscosity of a supercritical fluid is about 100 times lower than a liquid. With similar density to that of a liquid, the lower viscosity helps to develop turbulent flow in tubings of systems using supercritical fluids, preventing laminar flow dispersion of separated components. More importantly, the very low surface tension of supercritical fluids allows facile penetration into microporous and mesoporous materials to occur. All of the above factors favor the overall mass transfer in extraction using supercritical fluids to be faster than in the systems using liquid solvents. This is the reason why supercritical fluid extraction systems offer higher throughput than liquid solvent extraction systems.

As a result, SFE has several advantages over the conventional liquid phase extraction. Firstly, SFE is fast (its operation usually requires 1 to 3 hours) because of faster mass transfer characteristics caused by higher solute diffusivities and lower

viscosities of supercritical fluids than those of liquid solvents. Secondly, the solvent strength of a supercritical fluid can easily be controlled because the solubility depends on the pressure and temperature, whereas those of the liquid phase extraction could hardly be changed. Thirdly, many commonly used supercritical fluids are gaseous under ambient conditions, and the solute separation and concentration processes after SFE are greatly simplified. Fourthly, SFE using supercritical CO₂ is an environmentally safe process as it eliminates toxic gas emissions associated with calcination, it does not generate large amount of liquid waste solvents, and the exposure of operators to toxic solvents can be avoided.

Based on these superior properties, supercritical fluid extraction have been applied in numerous industrial applications [extensive review of SFE patents was done by M. A. McHugh and V. J. Krukonis, "Supercritical Fluid Extraction: Principles and Practice", 2nd Edition, Butterworth-Heinemann, 1994]. For examples, SFE process has been used for separations of mixtures of substances [U.S. Pat. 3,969,196], extraction of caffeine from coffee beans [U.S. Pat. No. 4,247,570], extraction of fat from starch-containing vegetable matter [U.S. Pat. No. 3,939,281], extraction of nicotine from tobacco [U.S. Pat. No. 4,153,063], densification of ceramic materials [U.S. Pat. No. 4,552,786], formation of transparent aerogel insulating arrays [U.S. Pat. No. 4,610,863], impregnation of polymer into wood to improve hardness and strength [U.S. Pat. No. 4,992,308], chemical vapor deposition for making thin film superconductors [U.S. Pat. 4,970,093], etc.

The current invention employs supercritical fluid CO₂ as the extraction solvent. Supercritical fluid CO₂ is the most commonly used supercritical fluid because it is inexpensive, nontoxic, nonflammable, and has relatively low critical temperature (31.3°C), and pressure (72.9 atm). Although pure supercritical CO₂ is a good extraction medium for

nonpolar and moderately polar species, it is less suitable for more polar compounds. Organic modifiers (also called cosolvent) are usually added into the flowing stream of supercritical fluid CO₂ in order to improve its polarity and extraction strength when extracting polar compounds.

Particularly, the present invention employing supercritical fluid CO₂ is uniquely beneficial in extracting the templated surfactants from a particular embodiment of synthetic porous materials, which particular embodiment is referred to hereinafter as M41S materials. M41S materials, a series of mesoporous molecular sieve materials recently discovered by Mobil scientists [U.S. Pat. 5,057,296], have very uniform mesopores (with pore diameters adjustable from 13 to 100 Angstroms) and have very high surface areas (> 1,000 m²/g). These mesoporous materials have gained world-wide attention as potential catalysts and adsorbents. Synthesis of M41S materials requires a large amount of surfactants as templating agents for the creation of the mesopores; in fact, more than 50% of the overall weight of the freshly synthesized MCM-41 material, a member of the M41S family, is due to the templated surfactant. As the surfactant is an expensive chemical, the present invention provides a fast, non-destructive, and environmentally safe extraction process to recover and recycle the expensive surfactant from the mesopores of M41S materials, hence reducing substantially the production cost of M41S materials.

SUMMARY OF THE INVENTION

The present invention provides a method to remove and recover a templating surfactant agent from a freshly synthesized synthetic porous material having said

templating agent sorbed within pores of said synthetic porous material comprising the steps of:

(a) contacting said freshly synthesized synthetic porous material with a flow of supercritical fluid with or without containing a certain amount of organic modifier, wherein the flowrates of said supercritical fluid and organic modifier are controlled by high pressure liquid pumps as shown in **FIG. 1** and the operating temperature and pressure are controlled to keep said supercritical fluid and organic modifier in the supercritical state.

(b) holding said synthetic porous material, said flows of supercritical fluid and organic modifiers at said elevated temperatures and pressures for a period of time sufficient enough to extract at least a portion of said templating agent from said freshly synthesized synthetic porous material.

(c) separating said extracted templating agent and said organic modifier from said synthetic porous material at atmospheric pressure and a predetermined temperature and collecting the said extracted templating agent and said organic modifier using a collector.

Suitable supercritical fluid used as extracting solvent in the present invention may be any supercritical fluids with moderate critical temperature and pressure, preferably supercritical fluid CO₂ because it is cheap, non-toxic, easy to handle and has low critical temperature and pressure. Operating temperature is preferably from 45 °C to about 125 °C, more preferably at about 85 °C. Operating pressure is preferably from 150 bar to 400 bar, more preferably at about 350 bar. The organic modifier may comprise of any polar organic solvents, preferably methanol or ethanol.

This invention is particularly beneficial in extracting templating surfactant agents from the pores of a type of mesoporous materials, referred hereinafter as M41S materials,

particularly MCM-41 materials. MCM-41, one of the members of this extensive family, is a porous inorganic material having uniform, hexagonally-arranged pores with pore diameters adjustable from about 13 to 100 Angstroms and exhibiting a hexagonal electron diffraction pattern that can be indexed with a d_{100} value greater than 18 Angstrom Units.

Particularly, this invention characterizes the templating surfactant agents extracted out from the pores of said porous materials by means of thermal gravimetric analysis, differential thermal analysis, infrared spectroscopy, and gas chromatograph/mass spectroscopy. The present invention shows that said extracted templating agent obtained from said SFE process retain the same chemical structure as the fresh surfactant, proving said SFE process a non-destructive extraction method and said extracted templating agent viable for recycle. Additionally, X-ray diffraction and N_2 adsorption data prove that said porous material treated by said SFE process retains its porous structure.

DESCRIPTION OF DRAWINGS

FIG. 1 is a diagram of the experimental set-up for supercritical fluid extraction.

FIG. 2 are (a) nitrogen adsorption and desorption isotherms (filled mark-adsorption; empty mark- desorption) and (b) BJH pore size distribution of the calcined product of EXAMPLE 1.

FIG. 3 are X-ray diffraction patterns of the (a) freshly synthesized and (b) calcined product of EXAMPLE 1.

FIG. 4 is a thermal gravimetric analysis spectrum of the freshly synthesized product of EXAMPLE 1.

FIG. 5 is a differential thermal analysis spectrum of the freshly synthesized product of EXAMPLE 1.

FIG. 6 are (a) nitrogen adsorption and desorption isotherms (filled mark-adsorption; empty mark- desorption) and (b) BJH pore size distribution of the calcined product of EXAMPLE 2.

FIG. 7 are X-ray diffraction patterns of the (a) freshly synthesized and (b) calcined product of EXAMPLE 2.

FIG. 8 is a thermal gravimetric analysis spectrum of the freshly synthesized product of EXAMPLE 2.

FIG. 9 is a differential thermal analysis spectrum of the freshly synthesized product of EXAMPLE 2.

FIGS. 10-13 are thermal gravimetric analysis and differential thermal analysis spectra of the extracted products of EXAMPLE 4, EXAMPLE 8, EXAMPLE 9, and EXAMPLE 11, respectively.

FIG. 14 is an X-ray diffraction pattern of the extracted product of EXAMPLE 9.

FIG. 15 are thermal gravimetric analysis and differential thermal analysis spectra of the extracted product of EXAMPLE 12.

FIG. 16 is an X-ray diffraction pattern of the extracted product of EXAMPLE 12.

FIG. 17 are infrared spectra of the solid samples prepared from mixing KBr with the solid sample of (a) EXAMPLE 13 and (b) EXAMPLE 14.

FIG. 18 are gas chromatograph spectra detected by flame ionization detector on (a) the extract of EXAMPLE 9 and (b) the methanol solution of the solid sample of EXAMPLE 14.

FIG. 19 are mass spectra recorded at the peak positions (about 20 min) of gas chromatograph spectrum shown in FIG. 18 on (a) the extract of EXAMPLE 9 and (b) the methanol solution of the solid sample of EXAMPLE 14.

DETAILED DESCRIPTION

In the present invention, supercritical fluid extraction (SFE) is employed as a fast, environmental-friendly, and non-destructive method to efficiently extract templating surfactant agents from the mesopores of M41S materials. In one embodiment of the invention, the efficiency of extraction is increased by changing SFE operating conditions, such as temperature, pressure, flow rate, type of organic modifier, and by changing material composition, such as Si or Al framework content. In another embodiment of the invention, the mesoporous structures of the freshly synthesized and surfactant-extracted M41S materials are characterized by various characterization techniques to ensure the stability of M41S mesoporous structures under SFE process. In a further embodiment of the invention, the chemical structures of the extracted templating surfactant and of the fresh surfactant are characterized by various characterization techniques to confirm the stability of chemical structures of templating surfactants under SFE process at various operating conditions. In a preferred embodiment of the invention, the extracted surfactant template is recovered and recycled as the fresh surfactant in the synthesis of M41S materials.

Templating Surfactants

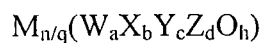
A templating surfactant is a certain type of organic compound which fills the pores of the freshly synthesized porous materials. The pores of said porous materials are only accessible after the templating surfactants are removed completely from the pores. The templating surfactants used in the syntheses of M41S materials are bulky organic bases, such as cetyltrimethylammonium (CTMA), myristyltrimethylammonium (C₁₄TMA), decyltrimethylammonium, etc.

Synthetic Porous Materials

The present invention can be used to provide an economical method to recover templating surfactants from the freshly synthesized porous materials, including zeolites and other similar molecular sieve materials. Additional molecular sieve materials which may be purified in accordance with the present invention include ZSM-4 (British Pat. No. 1,117,568); ZSM-5 (U.S. Pat. Nos. 3,702,886 and 4,100,262); aluminophosphates, such as ALPO-5, VPI-5, etc; and silicoaluminophosphates, such as SAPO-5, SAPO-37, SAPO-40, and SAPO-41 (which are variously taught in U.S. Pat. Nos. 4,440,871; 4,554,143; 4,666,875; and 4,742,033). More particularly, the method described in this invention is preferred for recovering surfactants from the freshly synthesized M41S mesoporous materials.

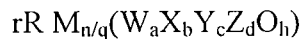
The syntheses of M41S mesoporous materials are taught in U.S. Pat. Nos. 5,057,296; 5,098,684; 5,108,725; 5,143,879 and other sources [see, for example Beck et al., "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates", Journal of American Chemical Society, 1992, volume 114, p10834]. The

M41S mesoporous materials, particularly MCM-41 has the following composition:



wherein W is a divalent element; X is a trivalent element, such as aluminium, iron; Y is a tetravalent element, preferably silicon; Z is a pentavalent element, such as phosphorus; M is one or more ions, such as ammonium, Group IA, IIA and VIIB ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; a, b, c and d are mole fractions of W, X, Y and Z, respectively; h is a number from 1 to 2.5 ; and (a+b+c+d) =1.

In the freshly synthesized form, the mesoporous material has a composition, on an anhydrous basis, expressed empirically as follows:



wherein R is the total organic material not included in M as an ion, and r is the coefficient for R, i.e., the number of moles or mole fraction of R.

The M41S materials can be distinguished from other porous inorganic solids by the regularity of its large open pores, whose pore diameter is in the range of 13 to 200 Angstroms. These mesoporous materials show characteristic X-ray diffraction pattern with a few distinct maxima in the extreme low angle region, which reflects the regular arrangement of the crystal lattice.

Supercritical Fluid Extraction

Generally, during supercritical fluid extraction, soluble analytes are partitioned from the matrix of the porous material into the supercritical fluid, then they are swept

through the back-pressure regulator into an extract collector operating at ambient pressure and a temperature above the extraction temperature. Based on this simple operation, a supercritical fluid extraction system is quite simple as it consists of only a few equipment [see, for example, Saito et al., "Fractionation by Packed-Column SFC and SFE: Principles and Applications," VCH, 1994]. A liquid pump supplies an extracting fluid to an extraction vessel at a constant flow rate and pressure. Another liquid pump (optional) supplies organic modifiers into the flowing stream of the extracting fluid at a constant flow rate and pressure. An extraction vessel holds the freshly synthesized porous material and is placed in a heater or in a water bath to maintain the extraction temperature above the critical temperature of the extracting fluid. A back-pressure regulator maintains the system at the supercritical pressure. An extract collector separates the extracted analytes from the supercritical fluid, and collects the extracted analytes into a glass vial.

The supercritical fluid extraction system of this invention is shown in **FIG 1**. The SFE system consists of a JASCO PU-980 liquid pump for introducing liquefied CO₂, a chiller (Polyscience) for liquefying CO₂, an ISCO 100DM syringe pump for introducing an organic modifier, a 10-ml extraction vessel, a water bath (Techne) for controlling the extraction temperature, a back-pressure regulator (JASCO 880-81 BPR), and an extract collector.

The SFE process of this invention is performed as follows. The extraction vessel, loaded with 1.0 gram of the freshly synthesized porous material, is connected into the SFE system. The extraction vessel and the mixer are then immersed in a water bath, which temperature has been set at the desired values. Liquid CO₂ is then pumped into the system at a flow rate of 1.0 ml/min. The organic modifier, if required to modify the polarity of the supercritical fluid, may also be pumped into a mixer to mix with the supercritical fluid

CO₂. The supercritical fluid CO₂, together with the organic modifier, passes through the extraction vessel and extracts the templating surfactant from the porous materials. The extracted surfactant dissolved in the supercritical fluid is then separated from the supercritical fluid CO₂ at the outlet of the back-pressure regulator and is collected at the extract collector. The extracted sample is dried at room temperature for overnight and stored in a vial for further characterization.

Characterization of Surfactants and Porous Materials

To further illustrate that the SFE process of this invention is a non-destructive method for extracting the surfactant template from the pores of porous materials, the extracted surfactant samples and the porous materials which have gone through the SFE process are analyzed by several characterization techniques.

X-ray diffraction pattern is used to characterize the mesoporous structure of the freshly synthesized and surfactant-extracted porous materials in order to prove that SFE process does not damage the pore structure of the porous materials. X-ray diffraction pattern of this invention is recorded on a Shimadzu XRD-6000 diffractometer using Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) and a scan speed of 2 degrees/min at 40 kV and 30 mA. Powder samples are supported on an aluminium sample holder for measurement. Due to the limitation of the machine, scanning degree is started from 1.5 degree.

Nitrogen adsorption at 77 K is used to characterize the surface area and pore size distribution of porous materials. Based on the nitrogen adsorption data obtained in the partial pressure range of 0.05 to 0.25, the surface area of the porous material is calculated using a method developed by Brunauer, Emmett and Teller (BET) [S. Brunauer, P.H.

Emmett, and E. Teller, Journal of American Chemical Society, 1938, volume 60, p309]. BET has been widely used for characterizing the surface areas of porous materials. As the porosity of porous materials is reflected by the changes of adsorption-desorption isotherms, pore size distribution of porous materials can be derived using certain adsorption models to simulate pore filling by nitrogen adsorbate. The pore size distribution of porous materials calculated in the present invention is based on the method developed by Barrett, Joyner and Halenda (BJH) [E. P. Barrett, L. G. Joyner and P. P. Halenda, Journal of American Chemical Society, 1951, volume 73, p373]. Desorption isotherm is preferably used in the calculation of BJH pore size distribution as it exhibits, for the same volume of adsorbate, a lower relative pressure than the adsorption isotherm, resulting in a lower free energy state or closer to true thermodynamic stability.

In the present invention, nitrogen adsorption is carried out on a Quantachrome NOVA 1000 analyzer. Samples (0.02-0.1 grams) are pretreated in flowing nitrogen at 300°C (or at other temperatures) for 1 hour prior to the adsorption measurement. Adsorption and desorption isotherms are measured in the partial pressure (P/P^0) range of 0.05-0.95. Surface area is determined from the adsorption data in the partial pressure range of 0.05-0.25 using multi-point BET method. Pore size distribution is determined from the desorption isotherm using BJH method.

Thermal gravimetric analysis is used to characterize the amount of surfactant that has been extracted from the freshly synthesized porous materials; this is done by comparing the loss amount of surfactant from the freshly synthesized porous materials and those after supercritical fluid extraction. Typically, two steps of weight losses are observed on freshly synthesized pure siliceous M41S materials, while three steps of weight losses are observed on freshly synthesized alumino-siliceous M41S materials. The first-

step weight loss obtained at temperatures below 140 °C is due to the loss of water from the pores. The second-step weight loss obtained at temperatures between 150-380 °C is due to the removal of the templating surfactants associated with the surface silanol groups of the mesopores. The third-step weight loss obtained between 380 and 700 °C, which is observed only with alumino-siliceous M41S materials, is due to the removal of the templating surfactants associated with surface Al sites. Based on these results, the second-step weight loss measures the amount of surfactant templated in the pores of pure siliceous M41S materials, and the sum of the second-step and third-step weight losses measures the amount of surfactant templated in the pores of alumino-siliceous M41S materials. The extraction efficiency using SFE method is expressed as the percentage of the amount of surfactant that has been extracted from the materials to the total amount of surfactant in the freshly synthesized sample. This calculation is based on the fact that the total amount of silica and alumina in the sample remains constant during thermal gravimetric analysis measurement. Simultaneously coupled with thermal gravimetric analysis, differential thermal analysis, which is based on the exothermic or endothermic thermal changes with temperatures of the desorbing organic or inorganic species from the pores, is especially useful for identifying the types of surface species attached in the pores.

In the present invention, thermal gravimetric analysis and differential thermal analysis are performed simultaneously using a Shimadzu DTG-50 Thermal Analyzer. The flow rate of air to the system is set at 40 ml/min and the temperature of the sample in the sample holder is ramped at a rate of 20 °C/min from room temperature to 800 °C. Alpha-alumina is used as a standard reference during differential thermal analysis measurement.

To further illustrate the nature of this invention, the following examples are presented. It should be understood that the invention is in no way limited to these specific

examples.

EXAMPLE 1

A 402.0 gram quantity of cetyltrimethylammonium hydroxide (CTMAOH) solution (20.8 wt. %), which was prepared by exchanging 20 wt. % of cetyltrimethylammonium bromide (CTMABr) solution with a hydroxide-for-halide exchange resin and then followed by condensation to 20.8 wt. %, was mixed with 17.0 grams of fumed silica (Aerosil 200) under constant stirring to form a slurry. The slurry, after being stirred for about 6 hours at room temperature, was transferred to polypropylene bottles and was then treated at 96 °C for 48 hours. The resulting solid was recovered by centrifuge, washed with deionized water, and dried at 50 °C overnight. The resulting dried solid is referred to hereinafter as freshly synthesized Si-MCM-41. Part of the freshly synthesized Si-MCM-41 was calcined in air at 550°C for 10 hours in order to thermally remove the templating surfactant from the mesopores; the calcined solid is referred to hereinafter as calcined Si-MCM-41.

Based on the data of nitrogen adsorption at 77 K, the calcined Si-MCM-41 proved to have a BET surface area of 1295 m²/g and a sharp BJH pore diameter distribution centered at about 30 Angstroms. **FIG. 2** shows the nitrogen adsorption and desorption isotherms and the BJH pore size distribution of the calcined Si-MCM-41. The type IV adsorption and desorption isotherms are typical of those mesoporous materials; the adsorption at low P/P^0 is due to the monolayer adsorption of N₂ on the wall of mesopores and on the external surfaces, and the steep increase at P/P^0 around 0.3 is due to the Kelvin condensation of liquid N₂ in the mesopores.

The X-ray diffraction patterns of the freshly synthesized and calcined Si-MCM-41

are shown in **FIG. 3**. The freshly synthesized Si-MCM-41 shows a very strong relative intensity line at a d-spacing around 42.1 ± 2.0 Angstroms and a weak line at a d-spacing around 21.6 ± 1.0 Angstroms. The calcined Si-MCM-41 shows characteristic lines at d-spacings around 37.6 ± 2.0 Angstroms and around 19.6 ± 1.0 Angstroms. The d-spacings of the calcined Si-MCM-41 are comparatively lower than those of the freshly synthesized Si-MCM-41, indicating that the mesopores contracted after the templated surfactant was thermally removed from the mesopores.

The thermal gravimetric analysis spectrum of the freshly synthesized Si-MCM-41 is shown in **FIG. 4**. The first-step and second-step weight losses observed on the thermal gravimetric analysis spectrum are due to the losses of water and surfactant, respectively. It is found that over 50% of the total weight of the freshly synthesized Si-MCM-41 is attributed to the templating surfactant in the mesopores.

FIG. 5 shows the differential thermal analysis spectrum (collected simultaneously as thermal gravimetric analysis) of the freshly synthesized Si-MCM-41. The two small endothermic peaks observed at temperatures lower than 200°C are due to the desorption of water and the decomposition of templated surfactant. The intense exothermic peak at about 350°C is due to the combustion of templated surfactants in air.

EXAMPLE 2

A 15.6 gram quantity of water was mixed with 1.96 grams of NaAlO_2 , 37.6 grams of TEAOH (tetraethylammonium hydroxide, 20 wt. %), and 38.4 grams of Ludox (Du Pont, 40% colloidal silica in water). After stirring the mixture at room temperature for 30 minutes, 84 grams of cetyltrimethylammonium hydroxide (CTMAOH) solution (20.8 wt.

%) prepared as in EXAMPLE 1 was added in drops into the mixture. The resulting slurry was stirred for another 2 to 3 hours before it was transferred to polypropylene bottles. The reaction mixture was then thermally treated at 96°C for 48 hours. After hydrothermal treatment, the solid product was recovered by centrifuge, washed completely with deionized water, and dried at 50 °C overnight. The resulting dried solid product (with a Si/Al molar ratio of 10), which is referred to hereinafter as freshly synthesized Si-Al-MCM-41, was stored in sample bottles for further investigation. Other freshly synthesized Si-Al-MCM-41 samples with different Si/Al molar ratios were similarly obtained using the above synthesis procedures by adjusting the amount of NaAlO₂ in the starting synthesis mixture. Similar to EXAMPLE 1, part of the freshly synthesized Si-Al-MCM-41 sample was calcined at 600 °C for 10 to 20 hours in order to remove the templating surfactant from mesopores; the calcined product is referred hereinafter as calcined Si-Al-MCM-41.

Based on the data of nitrogen adsorption at 77 K, the calcined Si-Al-MCM-41 proved to have a BET surface area of 1292 m²/g and a sharp BJH pore diameter distribution centered at about 30 Angstroms. **FIG. 6** shows the nitrogen adsorption and desorption isotherms and the BJH pore size distribution of the calcined Si-Al-MCM-41. Both the isotherms and the pore size distribution of the calcined Si-Al-MCM-41 are similar to those of the calcined Si-MCM-41; all of these isotherms are typical of MCM-41 mesoporous materials.

The X-ray diffraction patterns of the freshly synthesized and calcined Si-Al-MCM-41 are shown in **FIG 7**. The freshly synthesized Si-Al-MCM-41 shows a very strong relative intensity line at a d-spacing of 42.1 ± 2.0 Angstroms and weak lines at d-spacings around 23.3 ± 1.0 and 21.0 ± 1.0 Angstroms. The calcined Si-Al-MCM-41 shows characteristic lines at d-spacings around 39.4 ± 2.0 Angstroms and around 21.0 ± 1.0

Angstroms. The contraction of mesopores due to the thermal removal of templating surfactant was also observed on the calcined Si-Al-MCM-41, similar to the calcined Si-MCM-41.

The thermal gravimetric analysis spectrum of the freshly synthesized Si-Al-MCM-41 is shown in **FIG. 8**. Three steps of weight losses observed at temperatures between 40 to 800 °C are due to the losses of adsorbed water, Si-associated templating surfactant, and Al-associated templating surfactant, respectively. Compared with the thermal gravimetric analysis results of the freshly synthesized Si-MCM-41, freshly synthesized Si-Al-MCM-41 obviously needs a higher calcination temperature to remove completely the templating surfactant from mesopores. It is also found that about 50% of the total weight of the freshly synthesized Si-Al-MCM-41 is attributed to the surfactant templated in the mesopores, similar to the freshly synthesized Si-MCM-41.

FIG. 9 shows the differential thermal analysis spectrum of the freshly synthesized Si-Al-MCM-41. The intense exothermic peak observed at about 350 °C is due to the combustion of templating surfactants in air. Compared with the differential thermal analysis spectrum of the freshly synthesized Si-MCM-41, freshly synthesized Si-Al-MCM-41 particularly shows some exothermic processes at temperatures above 500 °C, which are attributed to the difficulty in removing these templating surfactants associated with Al sites.

EXAMPLE 3

In this example, pure supercritical fluid CO₂ (with no organic modifier) was used to extract the templating surfactant from the mesopores of the freshly synthesized Si-MCM-41 material of EXAMPLE 1. The extraction was carried out with about 1.0 gram of the

freshly synthesized Si-MCM-41, with a liquid CO₂ flow rate of 1.0 ml/min, at a temperature of 85 °C, and at a pressure of 350 bar. The chosen operating temperature and pressure maintain CO₂ in the supercritical fluid state. After 3-hr extraction, the surfactant-extracted Si-MCM-41 was unloaded from the extraction vessel.

The amount of templating surfactant still left in the mesopores of the surfactant-extracted Si-MCM-41 of this example was measured by thermal gravimetric analysis. The extraction efficiency was calculated based on the loss amount of surfactant between 150 °C and 400 °C. The loss amount of surfactant measured by thermal gravimetric analysis for both the freshly synthesized Si-MCM-41 and the surfactant-extracted Si-MCM-41 of this example is the same, indicating that pure supercritical fluid CO₂ was not polar enough to extract the polar templating surfactant, i.e. cetyltrimethylammonium hydroxide (CTMAOH), from the mesopores of the freshly synthesized Si-MCM-41. Therefore, supercritical fluid CO₂ needs to be modified with some polar organic modifier in order to achieve sufficient polarity to extract the polar templating surfactants from mesopores of M41S materials.

EXAMPLES 4-11

In EXAMPLES 4 - 11, supercritical fluid CO₂ modified with a polar organic modifier was used to extract the templating surfactant from freshly synthesized Si-MCM-41 material of EXAMPLE 1. The organic modifier was introduced at a certain flow rate and mixed with the flowing stream of supercritical fluid CO₂. In all these examples, the 3-hour extraction was carried out with about 1.0 gram of the freshly synthesized Si-MCM-41 at a pressure of 350 bar, and the extract was collected in a glass vial. The extraction efficiency was calculated based on the difference of the loss amount of surfactant during

thermal gravimetric analysis on the freshly synthesized and the surfactant-extracted samples at temperatures between 150 °C and 400 °C.

Materials	Temp. (°C)	modifier	modifier flow (ml/min)	H ₂ O content (%)	surfactant (%)	surfactant removed (%)
EXAMPLE 1	-	-	-	5.8	53.6	-
EXAMPLE 4	85	ethanol	0.1	4.4	26.5	70.9
EXAMPLE 5	85	ethanol	0.2	3.3	16.0	85.0
EXAMPLE 6	85	ethanol	0.3	3.3	14.8	86.3
EXAMPLE 7	75	ethanol	0.2	4.9	30.2	64.8
EXAMPLE 8	65	ethanol	0.2	3.9	31.8	62.6
EXAMPLE 9	85	methanol	0.1	4.8	8.5	92.6
EXAMPLE 10	85	methanol	0.2	3.7	21.2	92.5
EXAMPLE 11	85	methanol	0.3	5.7	13.7	87.1

To demonstrate that substantial amount of the templating surfactant had been removed by the SFE method of the present invention, the surfactant-extracted Si-MCM-41 samples of EXAMPLES 4, 8, 9, and 11 were characterized by thermal gravimetric analysis and differential thermal analysis, as shown in **FIGS. 10, 11, 12, and 13**, respectively. **FIGS. 10 – 13** clearly show that both the amount of surfactant lost in thermal gravimetric analysis and the differential thermal analysis signal become much smaller for all the surfactant-extracted Si-MCM-41 samples of these examples, strongly showing that supercritical fluid CO₂ modified with polar organic modifier was successful in extracting most of the templating surfactant from the mesopores of the freshly synthesized Si-MCM-41.

The X-ray diffraction pattern of the surfactant-extracted Si-MCM-41 of EXAMPLE 9 (**FIG. 14**) is in good agreement with those of the freshly synthesized Si-MCM-41 (**FIG. 3**). The X-ray diffraction data show that MCM-41 mesoporous structures were not damaged under SFE processing condition.

In accordance with the present invention, it has been found in these examples that

the addition of a small amount of either ethanol or methanol to supercritical fluid CO₂ greatly enhances the extraction efficiency, with methanol being a better organic modifier than ethanol. In addition to the enhancement of the extraction efficiency by organic modifiers, many other SFE operating parameters (such as temperature, pressure, and modifier flow rate) may also be used to enhance the extraction efficiency. For an example, under a constant flow rate of ethanol (0.2 ml/min), the extraction efficiency was increased from 62.6 % to about 85 % when the extraction temperature was increased from 65 °C (shown in EXAMPLE 8) to 85 °C (shown in EXAMPLE 5), showing that the solvating power of the supercritical fluid CO₂ modified with ethanol increases with extraction temperature. Methanol and ethanol showed quite different extracting behavior when their flow rates were changed. Ethanol showed a monotonous increase of the extraction efficiency when its flow rate was increased from 0.1 to 0.3 ml/min, whereas methanol showed the reverse trend. In fact, methanol had the highest extraction efficiency when its flow rate was set at 0.1 ml/min (shown in EXAMPLE 9); the highest extraction efficiency for freshly synthesized Si-MCM-41 was found to be 92.6 % under the SFE operating conditions of EXAMPLE 9.

EXAMPLE 12

One gram of the freshly synthesized Si-Al-MCM-41 material of EXAMPLE 2 was loaded into the extraction vessel. Supercritical fluid extraction was performed on this sample under the following operating conditions: sample amount – 1.0 gram, liquid CO₂ flow rate - 1.0 ml/min, methanol flow-rate - 0.2 ml/min, temperature - 85 °C, and pressure - 350 bar. After 3-hour extraction, the surfactant-extracted Si-Al-MCM-41 was collected

from the extraction vessel.

material	Temp. (°C)	modifier	modifier flow (ml/min)	H ₂ O content (%)	surfactant (%)	surfactant removed (%)
EXAMPLE 2	-	-	-	4.2	44.3	-
EXAMPLE 12	85	methanol	0.2	3.4	22.3	65.1

The thermal gravimetric analysis and differential thermal analysis spectra of the surfactant-extracted Si-Al-MCM-41 of this example are shown in **FIG. 15**. Compared with the relative loss amount of surfactant of the freshly synthesized and surfactant-extracted Si-MCM-41 (**FIGS. 4 and 12**), and based on the loss amount of surfactant from the freshly synthesized Si-Al-MCM-41 (**FIG. 8**), the surfactant-extracted Si-Al-MCM-41 of this example contains relatively larger amount of unextracted templating surfactant in the mesopores. Additionally, compared with the exothermic peak of the differential thermal analysis spectra of the freshly synthesized and surfactant-extracted Si-MCM-41 (**FIGS. 4 and 12**), and based on the exothermic peak of the freshly synthesized Si-Al-MCM-41 (**FIG. 8**), the surfactant-extracted Si-Al-MCM-41 of this example similarly contains relatively larger amount of unextracted templating surfactant in the mesopores (**FIG. 15**). These results show that the templating surfactant associated with Al sites is also harder to extracted by the SFE process.

The results of this example are in good agreement with those of EXAMPLE 2, wherein higher calcination temperature was needed to thermally remove the templating surfactant associated with Al-sites. In agreement with this observation, the extraction efficiency on the freshly synthesized Si-Al-MCM-41 is found to be about 65.1%, which is

much lower than the extraction efficiency on the freshly synthesized Si-MCM-41. This is not surprising as the templating surfactants are more strongly connected to the frameworks of Si-Al-MCM-41. Similar results were also reported by Schmidt et al for liquid phase extraction, where only silanol-associated surfactant templates were successfully removed from the freshly synthesized Si-Al-MCM-41. This example shows that more powerful supercritical fluid CO₂ modified with organic modifiers (other than ethanol or methanol) is needed to completely extract the templating surfactant from Al sites of the freshly synthesized Si-Al-MCM-41.

The X-ray diffraction pattern of the surfactant-extracted Si-Al-MCM-41 (**FIG. 16**) agrees well with those of the freshly synthesized Si-Al-MCM-41 (**FIG. 7**). Obviously, there is no structural destruction of the Si-Al-MCM-41 material during SFE process.

EXAMPLE 13

Nine milliliters of the extract of EXAMPLE 9, containing both the volatile organic modifier (methanol) and the analyte (extracted surfactant), was transferred to a glass flask. The glass flask containing the extract was evacuated using a mechanical pump to remove the volatile organic modifier from the extracted surfactant. Evacuation of the extract for about 30 minutes produced about 0.24 gram of dried solid product, which is the templating surfactant extracted out from the mesopores of the freshly synthesized materials. The solid sample was stored for further study.

As the organic modifier could be trapped by a liquid nitrogen trap placed between the pump and the flask, this example shows that the organic modifier could be easily collected and recycled as a fresh organic modifier. Hence no organic solvent waste is

created, offering the SFE process of this invention an environmental-friendly recovering method for the templating surfactant in M41S materials.

EXAMPLE 14

Ten grams of the cetyltrimethylammonium hydroxide (CTMAOH) solution (20.8 % in water) prepared as in EXAMPLE 1 was evacuated under the same conditions as those sample in EXAMPLE 13 in order to remove the solvent (water). About 2.0 grams of the resulting solid sample, which is pure cetyltrimethylammonium hydroxide (CTMAOH), was obtained and was used as a reference surfactant in the characterization of the extracted surfactant.

EXAMPLE 15

Characterization by infrared spectroscopy

One of the most important aim of this invention is to recover and to recycle the organic templating agents. To further illustrate that the extracted surfactant has the same chemical structure as the fresh surfactant, Fourier transform infrared spectroscopy (FTIR) was used to characterize the chemical structures of the extracted compounds.

Two solid samples of this example were obtained from samples of the extracted solid samples of EXAMPLE 13 and EXAMPLE 14 by mixing and grinding them with KBr in order to have a sample/KBr weight ratio of 1/100. Each pellet used for FTIR measurement was prepared by pressing 0.4 gram of mixed sample under a pressure of 4

tons. Infrared spectra were recorded on a Shimadzu FTIR 8101M spectrometer in the range of 400-4000 cm^{-1} at a resolution of 4 cm^{-1} .

FIG. 17 shows the FTIR spectra of both samples. The excellent agreement between the infrared spectra of the samples made from the samples of EXAMPLE 13 and EXAMPLE 14 confirms their structural consistency. Unfortunately, the most characteristic bands for tertiary amines, which have the antisymmetric and symmetric C-N stretching modes, are only Raman active as suggested by Bellamy (see, for example, L. J. Bellamy, “The Infrared spectra of complex molecules”, vol 1, 3rd ed., Chapman and Hall, London, 1975, 288), and were not characterized by infrared spectroscopy.

EXAMPLE 16

Characterization by gas chromatograph - mass spectroscopy

To even further illustrate that the extracted surfactant maintains its chemical structure under SFE process, gas chromatograph - mass spectroscopy (GC-MS) technique was also used to characterize the chemical structures of the extracted surfactant. Experiments were performed on an HP 6890 GC-MS system equipped with a standard HP-5MS capillary column (5% phenyl methyl siloxane, 30.0m x 250 μm x 0.25 μm). The GC oven temperature was set at 120 °C and the carrier gas (He) flow rate was set at 1 ml/min. Generally, a single injection requires 5 μl of liquid sample. Products were analyzed either by a flame ionization detector (FID) or by a mass spectrometer.

The extract solution was obtained directly from the extract of EXAMPLE 9 (without having methanol solvent removed). Moreover, the reference solution was a methanol solution of the solid sample of EXAMPLE 14 prepared by dissolving 1.0 gram of

pure solid CTMAOH of EXAMPLE 14 in 20.0 grams of methanol. **FIG. 18** shows the GC chromatograms of both the extract and the reference sample. The intense peak at a retention time of about 1.2 minutes for both samples was analyzed by mass spectroscopy and was found to be due to solvent (methanol). Beside methanol peak, another peak at a retention time of about 20 minutes was observed on both spectra, which might indicate the presence of the same surfactant in both samples. In fact, **FIG. 19** shows that the mass spectra derived from these two peaks (at a retention time of about 20 minutes) for both samples are identical. The similarity in the GC retention time and the mass spectra for these two peaks of the two samples suggests strongly that they are of the same surfactant. Based on the FTIR results of EXAMPLE 15 and GC-MS results of this example, it is concluded that the surfactant extracted from the mesopores of Si-MCM-41 of EXAMPLE 1 maintains its original surfactant structure, even after it has gone through a cycle of synthesis as a template and extraction by SFE.

All of the results of the above examples (EXAMPLES 1- 16) clearly show that the SFE process of this invention offers a non-destructive extraction method to extract the templating surfactant with its chemical structure intact from the mesopores of MCM-41 materials. Hence, SFE offers a fast and environmental-friendly extraction method to recover and recycle the expensive templating surfactant in the synthesis of M41S mesoporous materials. Using the SFE method of the present invention, the production cost of M41S materials or other related porous materials could now be substantially reduced, and the commercial application of M41S materials or other new porous materials could be realized.

CLAIMS

1. A method of supercritical fluid extraction for removing at least part of the total templating agent from a porous synthetic material having said templating agent sorbed within pores of said synthetic material comprising:
 - a. providing a stream of supercritical fluid at a predetermined temperature and a predetermined pressure;
 - b. contacting said porous synthetic material with said supercritical fluid with or without a modifier or cosolvent for a predetermined period of time in a manner such that at least part of the templating agent is detached from the porous synthetic material; and
 - c. separating said extracted templating agent with or without said modifier or cosolvent from said porous synthetic material.
2. The method of claim 1, wherein said templating agent is a surfactant.
3. The method of claim 2 wherein said surfactant is an alkyltrimethylammonium salt.
4. The method of any one of the preceding claims, where the porous synthetic material is M41S material.
5. The method of claim 4, wherein said M41S material is pure Si-MCM41 material.
6. The method of claim 4, where said M41S material is Si-Al-MCM41 material.
7. The method of any one of the preceding claims, wherein the supercritical fluid is carbon dioxide.
8. The method of any one of the preceding claims, wherein said modifier or cosolvent is a polar organic solvent.

9. The method of claim 8, wherein said polar organic solvent is methanol or ethanol.
10. The method of any one of the preceding claims, wherein said temperature is between 45 and 125⁰C, preferably 85⁰C.
11. The method of any one of the preceding claims, wherein said pressure is between 150 and 350 bar, preferably 350 bar.
12. The method of any one of the preceding claims, wherein said period of contact time between said supercritical fluid, said modifier or cosolvent and said porous synthetic material is from 0.5 to 6 hours.
13. The method of any one of the preceding claims, wherein the liquid flow rate of said supercritical fluid is 1 ml/min.
14. The method of any one of the preceding claims, wherein the flow rate of said modifier or cosolvent is from 0.1 to 0.3 ml/min.
15. The method of any one of the preceding claims, wherein said modifier or cosolvent is present from 5 to 30%, volume/volume, or modifier or cosolvent to supercritical fluid.
16. The method of any one of the preceding claims, wherein said modifier or cosolvent is separated from extracted templating agent by evacuation, trapped in a cold trap, and recycled.
17. A method for removing a templating agent from a porous synthetic material having said templating agent sorbed within pores of said synthetic material comprising:
 - a. contacting said porous synthetic material with a supercritical fluid at a predetermined temperature and pressure; and

- b. holding said porous synthetic material and said supercritical fluid with or without a modifier or cosolvent in contact for a period of time sufficient to desorb at least a portion of said templating agent from the said synthetic material; and
 - c. separating the desorbed templating agent with or without said modifier or cosolvent from said porous synthetic material.
18. The method of claim 17, wherein said templating agent is a surfactant.
19. The method of claim 18, wherein said surfactant is an alkyltrimethylammonium salt.
20. The method of any one of claims 17 to 19, wherein said synthetic porous material is M41S material.
21. The method of claim 20, wherein said M41S material is pure Si-Al-MCM-41 material.
22. The method of claim 20, wherein said M41S material is Si-MCM-41 material.
23. The method of any one of claims 17 to 22, wherein said supercritical fluid is carbon dioxide.
24. The method of any one of claims 17 to 23, wherein said modifier or cosolvent is a polar organic solvent.
25. The method of claim 24, wherein said polar organic solvent is methanol or ethanol.
26. The method of any one of claims 17 to 25, wherein said temperature is between 45 and 125°C, preferably 85°C.
27. The method of any one of claims 17 to 26, wherein said pressure is between 150 and

350 bar, preferably 350 bar.

28. The method of any one of claims 17 to 27, wherein said period of contact time between said supercritical fluid, said modifier or cosolvent and said porous synthetic material is from 0.5 to 6 hours.
29. The method of any one of claims 17 to 28, wherein the liquid flow rate of said supercritical fluid is 1 ml/min.
30. The method of any one of claims 17 to 29, wherein the flow rate of said modifier or cosolvent is from 0.1 to 0.3 ml/min.
31. The method of any one of claims 17 to 30, wherein said modifier or cosolvent is present from 5 to 30%, volume/volume, of modifier or cosolvent to supercritical fluid.
32. The method of claim 17, wherein said modifier or cosolvent is separated from templating agent by evacuation, trapped in a cold trap, and recycled.
33. The method of claim 32, further comprising separating the modifier or cosolvent from extracted templating agent and recycling the recovered modifier or cosolvent to contacting step (a).
34. The purified porous synthetic material when obtained by the extraction or desorption method as claimed in any one of the previous claims.
35. Purified M41S material when obtained by an extraction or desorption method as claimed in any one of claims 1 to 32.
36. Purified M41S material according to claim 34, comprising Si-Al-MCM-41 material.
37. Purified M41S material according to claim 34, comprising Si-MCM-41 material.

38. Templating agent when separated and recovered from the extraction or desorption method as claimed in any one of claims 1 to 32.
- 39 A method for removing templating agent from a porous synthetic material, substantially as hereinbefore described and illustrated with reference to the examples.
- 40 A method of supercritical fluid extraction for removing templating agent from a porous synthetic material, substantially as hereinbefore described and illustrated with reference to the examples.