(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 004 165 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
26.07.2023 Bulletin 2023/30

(21) Application number: **20785681.6**

(22) Date of filing: **11.09.2020**

(51) International Patent Classification (IPC):
C10L 7/04 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C10L 7/04

(86) International application number:
PCT/EP2020/075527

(87) International publication number:
WO 2021/048392 (18.03.2021 Gazette 2021/11)

(54) METHOD FOR MAKING A FUEL TABLET

METHODE ZUR HERSTELLUNG EINER BRENNSTOFFTABLETTE

MÉTHODE À PRODUIRE UN COMPRIMÉ DE CARBURANT

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **13.09.2019 GB 201913244**

(43) Date of publication of application:
01.06.2022 Bulletin 2022/22

(73) Proprietor: **University of Tartu**
50090 Tartu (EE)

(72) Inventors:
- **TIMUSK, Martin**
  50090 Tartu (EE)
- **JÄRVEKÜLG, Martin**
  50090 Tartu (EE)
- **KANGUR, Triin**
  50090 Tartu (EE)

(74) Representative: **Williams Powell**
44 Prospect Place
Bromley, Kent BR2 9HN (GB)

(56) References cited:
GB-A- 2 401 374
US-A1- 2006 051 627
US-A1- 2014 323 589

- **DATABASE WPI Week 201780 Thomson Scientific, London, GB; AN 2017-79702W XP002801216, & RU 2016 114606 A (SMOLYAKOV V G) 5 October 2017 (2017-10-05)**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Processed by Luminess, 75001 PARIS (FR)

Description

[0001] The present application relates to a method of preparing an inorganic alcogel for use as a source of fuel and to a fuel tablet (for example for a camping stove) which is obtainable from such a method.

[0002] Fuel tablets (particularly solid fuel tablets) are used in portable solid-fuel camping stoves for boiling water and preparing food and are distinct from liquid fuels like gasoline, propane and alcohols that require special burners. Fuel tablets find use in camping stoves for several reasons. Often natural fuel (e.g. wood) is not available, is not ignitable or no tools are available to process the wood into a usable form. Also, a source of fuel is often required which can be provided in an optimal size and can be quickly and reliably ignited irrespective of ambient conditions without requiring additional tools and apparatus. Solid and gel fuels are two general categories of non-natural fuels distinct from liquid fuels which can be rationed or processed into fuel tablet form.

[0003] Most common solid fuel tablets are based on hexamine (IUPAC name: 1,3,5,7-tetraazatricyclo[3.3.1.13,7] decane). Hexamine has a moderately high heat of combustion (30 MJ/kg) but has numerous disadvantages, which include:

- Hexamine is a tertiary amine and the tablets therefore have an intense unpleasant odour.
- Hexamine contains nitrogen and (in addition to carbon dioxide) its combustion additionally creates either formaldehyde, ammonia, nitrogen oxide or hydrogen cyanide, or a combination of these compounds.
- Ingestion of hexamine may cause nausea, vomiting, gastrointestinal disturbances and kidney damage.
- When burned, the fuel yields noxious fumes, requiring foods being cooked in tightly sealed cooking vessel.
- Burned tablets leave a sticky dark residue on the bottom of pots.

[0004] Often the so-called gel-mass or gel fuel products are considered to be solid fuels as these do not require special burners as liquid fuels do. In some cases, these are not gels but viscous polymer-alcohol solutions or thixotropic fluids, as disclosed for example in US 4157242 A (Energy & Mineral Research). According to the IUPAC definition, a gel is a non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid. Viscous or thixotropic liquids that are not gels by the correct definition can be called gel-mass products to make a distinction with true gels. In these products, the alcohol serves as fuel and other constituents are present as thickening agents. There are numerous different and distinct materials in a general category of "gel". These can be inorganic, organic, crosslinked and non-crosslinked, nanoparticle or polymer-based, biopolymer or synthetic polymer based, hydro- or alcogels and these materials can be prepared with methods ranging from simple mixing to complex chemical synthesis, yielding different chemical-, mechanical-, ion exchange- and rheological properties for different applications.

[0005] Gel-mass fuels based on alkyl-cellulose as an organic biopolymer gelling agent for alcohol have been proposed (see for example the disclosure in GB 2500062 A) and also true gels that do not exhibit flow at room temperature (see WO 2016/055814, which discloses a gel based on synthetic, crosslinkable organic polymer poly(acrylic acid) which is chemically crosslinked with poly(ethylene glycol dimethacrylate). These are examples of products where either an organic biopolymer or synthetic organic polymer is used either as thickening agent for alcohol or as true gel skeleton when crosslinked. Such materials are called "organic alcogels" where a network of organic polymer (with a hydrocarbon backbone) is filled throughout its whole volume by an alcohol. In cases in which an organic biopolymer or synthetic organic polymer is used either as thickening- or gelling agent for alcohol, the gelling agent is either partially combustible or decomposes during gel burning, which, in the last case does not result in clean burning and may release toxic fumes.

[0006] Typically gel-mass fuels contain a significant amount of water which is a required co-solvent for polymer thickener and alcohol (typically ethanol). As the heat of vaporization of water is quite high (2.257 MJ/kg), the water additive that remains in the alcogel reduces the overall heat of combustion of the alcogel since part of the energy released during burning is consumed by the evaporation of water.

[0007] The advantages of organic alcogel and gel-mass fuels in comparison to hexamine-based products are generally cleaner burning processes, reduced toxicity and a more pleasant odour when burnt. However, the viscosity of polymer solutions can be temperature-dependent, so gel-mass fuels can become more fluid under certain conditions which can result in safety issues. Also, organic polymer gelling agent decomposes or partially combusts, leaving residue and resulting in potentially harmful combustion products.

[0008] US 2006/051627 discloses alcogels as fuel compositions made from methanol as solvent and tetramethoxysilane as gel forming agent.

[0009] US 2008/0095928 A1 (GM Global Tech Operations Inc) discloses a coating including a silica-based material having pendent functional groups. In a specific example, it discloses a method of making a sol-gel from one part by weight of 1 N aqueous hydrochloric acid added to two parts N-(triethoxysilylpropyl) urea (50% in methanol) plus one part tetramethoxysilane.

[0010] This method is not suitable for use in producing a fuel tablet for a number of reasons:

(i) N-(triethoxysilylpropyl) urea as a precursor contains the propylurea functional group that is hydrolytically stable and is retained inside the material. If an alcogel was prepared from that precursor, the combustion of that gel would result in toxic combustion fumes due to nitrogen contained in the propylurea group.
(ii) Methanol is used as solvent, which is toxic.
(iii) 1N aqueous HCl is used as catalyst. This results in very low pH and very fast hydrolysis reactions of precursor alkoxides but at this acid concentration the sol is stable and either no gel formation occurs and no alcogel is obtained or gel formation time would be so long as to be commercially irrelevant.
(iv) The ratio of water to alkoxide in the specific example is 3.787. This is quite low and likely to result in soot formation if the product was combusted.

[0011] JP 2004022393 A (TDK Corp.) discloses a sol which is obtained from silica and/or an alkoxysilane and an alkoxysilane containing an alkoxyphosphoryl alkyl group. A gel is obtained from the sol, and the gel is heat-treated at a temperature of >100°C and <300°C. Through hydrolysis, a proton conductive electrolyte is obtained which is stable in a moistened state and durable in fuel cell operation.

[0012] CN 105037733 A (Univ. Wuhan) discloses a a phosphate siloxane high-temperature proton exchange membrane with hydrolytic stability and a preparation method thereof.

[0013] Other examples of fuel gel compositions are disclosed in GB 2401274 A (Barrett), WO 2016/055814 A1 (Air Global), and GB 2031018 A (Twente).

[0014] The present invention seeks to provide a method of preparation of an improved fuel tablet which seeks to mitigate at least some of the above disadvantages.

[0015] The invention is defined in the appended claims.

[0016] In a first aspect there is provided a method of preparing an alcogel for use as a source of fuel, including the steps of hydrolysing at least one tetraalkoxysilane with water in the presence of a solvent and catalyst, wherein the solvent includes at least one alcohol, and wherein the molar ratio (R) of water to tetraalkoxysilane is from 5 to 7. The realisation of the present application is that the hydrolysis of at least one tetraalkoxysilane in the defined conditions results in an alcogel which can be used as a source of fuel. Ideally, there are no alkoxysilanes present other than tetraalkoxysilanes. It has been discovered that mono/di/trialkoxysilanes do not form a suitable alcogel.

[0017] In preferred embodiments:

- The tetraalkoxysilane may be a combination of tetraethoxysilane (TEOS) and tetrapropoxysilane (TPOS).
- The solvent/fuel limited to ethanol, denatured ethanol, 1-propanol, 1,6-hexanediol, or any combination thereof.
- The solvent to tetraalkoxysilane volume ratio greater than 1:1, preferably greater than 2 and most preferably 2.3
- The molar ratio of water to tetraalkoxysilane is in the range of 5 - 7 (preferably equal to 6)
- The pH of the resulting gel is about 7. irrespective whether this value is held constant during the entire synthesis by using base catalysis with small concentrations of catalysts or hydrolysis is carried out at low pH and later pH being raised close to 7 for gel formation (that would otherwise not happen or would take months at low pH)
- The prepared alcogel is enclosed into hermetically sealed container to avoid evaporation of alcohol and the consequent loss of combustibility in alcogel transformation into dry amorphous oxide.

[0018] In general terms, the present invention discloses a method of preparation of an inorganic, sol-gel derived, SiO_2 skeleton-based alcogel as a fuel tablet. It has been discovered that silica-based (non-hydrocarbon backbone) alcogels combust and furthermore can safely burn in ambient atmosphere at a suitable rate to be usable as a clean-burning fuel tablet in portable solid-fuel camping stoves. Advantageously, the inventive fuel tablet produces no smoke, harmful chemicals or odours and produces only a small amount of pure, non-sticky silica in the form of an aerogel powder as a burning residue which can be easily discarded without recycling issues.

[0019] These aerogel powders have excellent properties in terms of density, average pore size and specific surface area and thus have value on their own. This is possibly the simplest route for preparing silica aerogel powders. A hydrolytic sol-gel process involving acid- or base catalyzed hydrolysis of metal- and silicon alkoxides is a well known and established field of chemistry with decades of detailed scientific research and thousands of scientific papers. There is vast number of known precursors in the form of silicon- and metal alkoxides as well as known processing steps of dip-, spin- and spray coating which were established decades ago. Despite this, innovation in the field of sol-gel chemistry has been continuous and significant.

[0020] Novel developments in the field of sol-gel chemistry can be achieved by relying on these known general principles and adding new, nontrivial processing steps to obtain structures and devices with novel and useful morphology or functionality. To illustrate this, from the known general knowledge of acid-or base-catalyzed hydrolysis and polycondensation reactions of silicon alkoxides it does not trivially follow for example that silica aerogel can be obtained. This requires complex processing steps beyond hydrolysis and polycondensation reactions of silica precursors. By adding novel processing steps and elaborating novel compositions, there is a great freedom to use hydrolysis and polycondensation reactions at different conditions and in combination with other distinct chemical reaction mechanisms and processing steps to prepare novel sols, nanoparticles, microspheres, foams, hydrogels and alcogels, phase separated microcomposites, fibers, xerogel monoliths/powders etc. with plethora of new properties and applications.

[0021] The two most common silicon compounds which are used in hydrolytic sol-gel process for obtaining silica-based materials are tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), the hydrolysis of which results in methanol and ethanol as reaction products, respectively. The hydrolysis reaction is typically accelerated by using an acid or base catalyst. TMOS is one of the few alkoxides that can undergo hydrolysis without using a catalyst. In case of TEOS, however, two types of catalysts are commonly used - ammonium hydroxide and ammonium fluoride. TMOS and TEOS compounds contain 4 alkoxy groups, capable of undergoing hydrolysis. Hydrolysis creates silanol (Si-OH) groups that can undergo polycondensation reaction with other Si-OH groups, resulting in water as a reaction product:

$$\text{Si-OH} + \text{HO-Si} \text{ -> } \text{Si-O-Si} + H_2O \qquad (1)$$

[0022] Alternatively, silanol groups may react with alkoxy groups (RO-Si), resulting an alcohol (ROH) as reaction product:

$$\text{Si-OH} + \text{RO-Si} \text{ -> } \text{Si-O-Si} + \text{ROH} \qquad (2)$$

[0023] It depends on the initial water to alkoxide ratio (R) whether reaction (1) or (2) dominates. If the water to alkoxide molar ratio is increased above 2, this increasingly results in water as a reaction product during silanol polycondensation. At R=2, the water-producing condensation reaction is statistically minimal and the polycondensation reaction between hydroxy- and alkoxy groups dominates, resulting in alcohol as reaction product. At R of around 4, the water-producing condensation reaction dominates. This creates 4 moles of water for every mole of silicon alkoxide which is retained inside the gel.

[0024] An alcogel forms when reacting and growing oligomeric species or nanoparticle chains reach the length of the reaction vessel, causing a loss of fluidity through polycondensation and thereby immobilizing the solvent. For preparation of aerogels from alcogel it is necessary to carry out solvent exchange multiple times, following the removal of solvent in supercritical conditions in order to avoid the collapse of pore structure due to capillary forces. At normal conditions gel cracking occurs as a result of compressive stresses caused by the existence of a meniscus at the liquid-vapor interface as solvents evaporate from the gel pores, resulting in differential capillary pressure and shrinkage of the gel. This leads to formation of a dense (and typically cracked) amorphous oxide material called xerogel. Thus, a preparation of an alcogel as well as its stable storage without the evaporation of alcohol from the gel pores inevitably requires an alcogel to be enclosed in hermetically sealed container. Otherwise the alcogel is transformed into an amorphous oxide. For example, spin-coating of sol does not result in an alcogel as an end-product as alcohol evaporates from the film. Any sol processing procedure that allows evaporation of alcohol does not result in an alcogel.

[0025] In a preferred embodiment therefore, the prepared alcogel is enclosed in a container to minimise the evaporation of alcohol and the consequent loss of combustibility in alcogel transformation into dry amorphous oxide. Most preferably, the container is hermetically sealed.

[0026] There are many known published aerogel synthesis protocols which describe the steps of preparation of silica aerogels by supercritical drying. Aerogel preparation includes an alcogel synthesis as an intermediate step in obtaining silica aerogel. This step is followed by time-consuming solvent exchange and supercritical drying of the wet gel to obtain an aerogel monolith.

[0027] One available example of prior art aerogel preparation protocol from TMOS as precursor is published online at http://www.aerogel.org/?p=1406 and also somewhat analogous aerogel synthesis protocol based on TEOS as precursor at https://www.aerogel.org/?p=1027. The synthesis was reproduced based on these protocols to determine their potential relevance in the context of the present invention. TMOS aerogel preparation protocol uses R-value of 4.146 with 0.0386 M NH_4OH as catalyst and alcohol to alkoxide volume ratio of 2 whereas TEOS-based aerogel preparation protocol uses R-value of 17.97 with 0.068 M NH_4OH and 0.0203 M NH_4F in aqueous solution as catalysts and alcohol to alkoxide volume ratio 4.4. The resulting heat of combustion values of these alcogels are about 17 MJ/kg and 20.9 MJ/kg respectively. These values are both relatively poor. For clarity, it is important to note that these gels are intermediate products for aerogel preparation and there is no prior information available about their burning properties. The combustibility of sol-gel derived alcogels is by no means trivially obvious and none of this has been described nor theorized in scientific- nor in patent literature. Furthermore, silica and some other inorganic oxides (e.g. Sb_2O_3) are known as flame retardants (DOI: 10.1002/1099-1018(200011/12)24:6<277::AID-FAM746>3.0.CO;2-A and DOI: 10.1007/978-94-011-5862-6_32). Additionally, in obtaining intermediate alcogel in case of aerogel preparation, there is no concern for solvent toxicity, heat of combustion, gel strength, influence of alcohols and catalysts on possible soot formation nor in toxicity of the respective combustion products. Instead, the optimization of the properties of the resulting aerogel is relevant, in terms of density, homogeneity, pore size distribution and the obtained specific surface area. The alcohol that is used in hydrolytic sol-gel process serves as co-solvent for alkoxide and water and is not treated as fuel.

[0028] The strength of the abovementioned alcogels are 10.62 N and 5.22 N respectively. The strength of the gel samples was determined by measuring force to failure by pressing a metal cylinder into an alcogel perpendicular to the axis of the cylindrical gel sample. This simulates the real-life situation of lifting the gel sample with fingers. The gel samples were geometrically identical and 27.3 mm in diameter. Strength below 5 N indicates very low strength, such that it is easy to break the gel just by trying to lift it by fingers and strength greater than 25 N is very good. Sol-gel derived alcogels do not reach their final strength immediately after gelation and in some cases weeks or months may be required to reach the final strength at room temperature. All samples were aged for at least three days, sufficient for relative comparison.

[0029] It is shown that in case of narrow, carefully selected and optimized composition range, cleanly burning (i.e. no soot formation, no toxic fumes) inorganic alcogel with suitable mechanical properties and with heat of combustion value at the level relevant to the practical applications is obtained. Alkoxides that can be used as precursors in preparation of an inorganic, sol-gel derived alcogels that are usable as cleanly burning fuel tablets, are strongly limited by their chemical structure. Only tetra-alkoxysilanes are usable, containing 4 alkoxy groups (Si-OR) attached to central silicon atom. Di- and tri-alkoxysilanes or any silicon alkoxide in general, that contains hydrolytically stable carbon-silicon bond is unsuitable for number of reasons -these alkoxides exhibit very low reaction rates and require high catalyst concentrations, almost universally induce phase separated sols and gels, result in very weak and poorly crosslinked gels, result in unclean burning and unclean burning residue and cause emanation of silica nano- and microparticles due to incomplete 3D SiO_2 skeleton formation at molecular level, posing a serious health hazard. Moreover, the choice of tetra-alkoxysilanes is also limited to compounds that only contain linear- or branched hydrocarbon-based alkoxy groups as only these result in cleanly burning alcohol formation at hydrolysis. Only when abovementioned requirements are fulfilled, an inorganic gel skeleton is incombustible and is thus fundamentally incapable of releasing toxic combustion fumes and the choice of alkoxides usable in an alcogel fuel tablet preparation is limited to TMOS, TEOS and tetrapropoxysilane (TPOS). All others are ruled out due to fundamental reasons stated above and out of these three, TMOS has very limited potential use.

[0030] In a preferred embodiment therefore, the tetraalkoxysilane may be a combination of TEOS and TPOS.

[0031] As methanol is poisonous, prior art TMOS-based alcogels as intermediates in obtaining aerogels and with no reported uses on their own, are unsuitable for use as fuel tablets as fuel tablets come in contact with skin and potential inhalation of methanol vapours poses serious health hazard. Also, TMOS/methanol combination yields low heat of combustion.

[0032] In general, TEOS is preferred over TMOS as it produces ethanol as the product of hydrolysis reaction. On the other hand, TEOS-based prior art aerogel preparation protocol uses large excess of water and yields mechanically weak alcogel. As hydrolysis of TEOS is very slow as compared to TMOS, the hydrolysis is incomplete at gel formation, even in the case of two different catalysts and this leads to phase separation. In aerogel preparation, this is overcome by using very high solvent concentration and large excess of water. This enables the avoidance of phase separation but very high solvent concentration results in weak gel.

[0033] Additionally, there is an aspect in alcogel preparation by sol-gel method that has never been considered as there has been no need or knowledge to address that issue scientifically nor technologically. Specifically, combustion of sol-gel derived alcogels yields soot when the flame comes into contact with a cold cooking vessel when higher aliphatic alcohols are used than methanol. The quantity of soot progressively increases as higher monohydroxy aliphatic alcohols are used as well as in case of increasing concentration of base catalysts, leading to higher pH values, away from 7.

[0034] Thus it is not possible to apply simple logic to just use alcohols with higher molecular weight (e.g ethanol, propanol etc.) in silica alcogels in order to increase the heat of combustion. These alcohols burn cleanly as liquids but in silica alcogel the alcohol is contained in micro- and mesopores where high pressures and temperatures during combustion (as well as the potential catalytic effect of the SiO_2 skeleton itself) partially converts alcohols into ethers and other compounds with high flash points, causing incomplete combustion and soot formation when the flame is cooled by a cooking vessel. The same applies to the R-value, which, in terms of maximum heat of combustion should be 2 (as the polycondensation mechanism dominates according to equation no. 2) but an R value of 2 is not optimal in terms of soot formation.

[0035] The composition of silica alcogels for use as fuel tablets is a balance therefore on the one hand between the toxicity of TMOS/methanol and on the other hand with soot formation in the case of higher aliphatic alcohols, with water- and catalyst concentration additionally influencing both heat of combustion and soot formation in a complex way. Due to heavy soot formation, TEOS-based alcogel with 1-propanol as added fuel can be used as firelighter, for example to start coal- or wood fire but is unsuitable for using as a fuel tablet in camping stoves. A preferred composition window can however be found which yields silica alcogel with suitable properties for using as fuel tablet in camping stove. This is achieved with TEOS-based alcogel, with ethanol as fuel, with a water to tetraalkoxysilane molar ratio of 5-6 and a reduced amount of catalyst to bring the final pH close to 7. As phase separation does not exhibit negative influence on alcogel fuel tablet, it is possible to work in a markedly different composition range as compared to TEOS-based aerogel preparation. Denatured ethanol can be used, containing denatonium benzoate as denaturant, as well as 96% ethanol by taking into account the water content for correct water to alkoxide molar ratio.

[0036] A pH value around 7 is preferred for minimal soot formation during combustion. This requirement is highly unconventional in the context of typical sol-gel process parameters that normally require a pH value away from neutral for the hydrolysis to occur. This is especially the case with TEOS. This poses serious limitations on the strategy of the use of catalysts and their concentrations. There are two possible options to meet this requirement: 1) The use of basic conditions with the use of NaOH, NH_4OH or other base catalyst in small concentration, enough to achieve gel formation in a commercially relevant timescale and in small enough amounts for minimal soot formation or 2) to use low pH (e.g. HCl as catalyst) for fast hydrolysis and raising pH close to 7 prior to packaging for fast gel formation by adding a strong base in water solution close to equimolar amount to the acid. The latter strategy thus involves the addition of water in two separate parts.

[0037] In one embodiment therefore, NH_4OH and NH_4F are used as catalysts for TEOS-based alcogel preparation with preferred molarity in aqueous solution in the range of 0.005-0.05 M and 0.003-0.03 M (most preferably 0.0067 M and 0.00327 M) for NH_4OH and NH_4F respectively. In the second embodiment tetraalkoxysilane is hydrolysed with HCl (preferably with an R value of 4 with 0.02 M HCl) and subsequently NaOH aqueous solution is added to raise pH close to 7 (preferably to the final R value of 6 with 0.04 M NaOH) to achieve gel formation.

[0038] In one embodiment, the volume ratio of solvent to tetraalkoxysilane is greater than 1:1, preferably greater than 2 and most preferably 2.3. The solvent may include ethanol, denatured ethanol, 1-propanol, 1,6-hexanediol, or any combination thereof and is preferably denatured ethanol.

[0039] In accordance with a second aspect of the present invention, there is provided a fuel tablet for a camping stove including an alcogel obtainable by means of a method as defined above which is contained in a container. For example, the container may be a paper-based wrapper that is impermeable to alcohols or a paraffin layer around the alcogel.

[0040] In accordance with a third aspect of the invention, there is provided a method of creating heat including the step of burning an alcogel as made by the above method or by removing a fuel tablet from the container as defined above and then burning it.

[0041] As well as creating heat, this method produces as a side product silica aerogel powder as a burning residue. This is a technically simple way of producing this product therefore.

[0042] In an alternative aspect of the invention, there is provided a method of preparing an alcogel for use as a source of fuel, including the steps of hydrolysing at least one silicon alkoxide with water in the presence of a solvent, wherein the solvent includes at least one alcohol, and wherein the molar ratio (R) of water to alkoxide is less than 4.

[0043] A number of preferred embodiments of the invention and counter examples (i.e. not within the scope of the invention) will now be described.

EXAMPLE 1

[0044] 27.4 mL of TEOS is added to 63 mL of denatured ethanol in a glass beaker and mixed for 1 minute. Consequently 13.35 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.0067 molar NH_4OH and 0.00333 molar NH_4F respectively) and mixed for 10 minutes. This results in water to alkoxide molar ratio of 6. Then, the sol is poured into polypropylene containers and sealed hermetically where gel formation takes place. Gel time is approximately 2 hours and 10 min at 22 °C and gel strength increases and reaches plateau in ~20 days at 22 °C. Silica alcogel is obtained with heat of combustion value of 23.4 MJ/kg. Gel formation and aging can be carried out at higher temperature up to the boiling point of alcohol to exponentially decrease gel time and accelerate aging without any drawback.

EXAMPLE 2

[0045] 27.4 mL of TEOS is added to 63 mL of denatured ethanol in a glass beaker and mixed for 1 minute. Consequently 13.35 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.00167 molar NH_4OH and 0.000833 molar NH_4F respectively) and mixed for 10 minutes. This results in water to alkoxide molar ratio of 6. Then, the sol is poured into polypropylene containers and sealed hermetically where gel formation takes place. Gel time is approximately 57 h at 22 °C and ~7.5 h at 50°C, representing an approximate higher limit at which the process is commercially relevant in terms of gel time that results from the used concentration of catalysts. The resulting silica alcogel has heat of combustion value of 23.4 MJ/kg, identical to Example 1.

EXAMPLE 3

[0046] 27.4 mL of TEOS is added to 63 mL n-propanol in a glass beaker and mixed for 1 minute. Consequently 13.25 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.0067 molar NH_4OH and 0.00333 molar NH_4F respectively) and mixed for 10 minutes. This results in water to alkoxide molar ratio of 6. Then, the sol is poured into polypropylene containers and sealed hermetically where gel formation takes place. Gel time is ~8 hours at 22 °C and gel strength continues to increase for over 7 days. This results in slightly turbid silica alcogel due to phase separation during gel formation. Alcogel with heat of combustion value of 27.5 MJ/kg is obtained.

EXAMPLE 4

[0047] 21.92 mL of TEOS and 3.65 mL of TMOS (9/1 molar ratio) is added to 63 mL of denatured ethanol in a glass beaker and mixed for 1 minute. Consequently 13.35 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.0067 molar NH_4OH and 0.00333 molar NH_4F respectively) and mixed for 10 min. This results in water to alkoxide molar ratio of 6. Then, the sol is poured into polypropylene containers and sealed hermetically where gel formation takes place. Gel time is approximately 3 h and 10 min at 22 °C.

EXAMPLE 5

[0048] 27.4 mL of TEOS is added to 30 mL 96% ethanol in a glass beaker and mixed for 1 minute. Consequently 7.418 mL of water is added that contains 0.05 M HCl as catalyst and mixed for 30 min. Consequently 3.709 mL of 0.1 M NaOH aqueous solution is added, mixed for 3 min, followed by addition of 33 mL of 96% ethanol. This results in water to alkoxide molar ratio of 6.13. Then, the sol is poured into polypropylene containers and sealed hermetically where gel formation takes place. Gel time is ~16 hours at 22 °C and optically clear and mechanically strong gel forms that contracts ~25% by volume during aging, expelling the equivalent amount of solvent, typical to acid-catalysed sols. The resulting gel strength is >2-3 times higher than those prepared by using base catalyst, reaching 30N. The strength of the gel samples was determined by measuring force to failure by pressing a metal cylinder into an alcogel perpendicular to the axis of the cylindrical gel sample that was lying horizontally on the flat surface. This simulates the real-life situation of lifting the gel sample with fingers. The gel sample was 27.3 mm in diameter

EXAMPLE 6

[0049] 27.4 mL of TEOS is added to 30 mL of denatured ethanol in a glass beaker and mixed for 1 minute. Consequently 11.043 mL of water is added (effectively R=5) that contains 0.02 M HCl as catalyst and mixed for 24 min. Consequently 0.552 mL of 0.4 M NaOH aqueous solution is added dropwise, mixed for 3 min, followed by addition of 33 mL of denatured ethanol. Then, the sol is poured into polypropylene containers and sealed hermetically where gel formation takes place. Gel time is ~10 hours at 22 °C and optically clear and mechanically strong gel forms that contracts ~18% by volume during aging.

EXAMPLE 7

[0050] 178.45 mL of tetrapropoxysilane (TPOS) is added to 315 mL of denatured ethanol in a glass beaker and mixed for 1 minute. Consequently 66.76 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.0067 molar NH_4OH and 0.00333 molar NH_4F respectively) and mixed for 10 minutes. This results in water to alkoxide molar ratio of 6. Then, the sol is poured into polypropylene containers and sealed hermetically where gel formation takes place.

EXAMPLE 8

[0051] 178.45 mL of tetrapropoxysilane (TPOS) is added to 315 mL of denatured ethanol in a glass beaker and mixed for 1 minute. Consequently 55.63 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.0067 molar NH_4OH and 0.00327 molar NH_4F respectively) and mixed for 10 minutes. This results in water to alkoxide molar ratio of 5. Then, the sol is poured into polypropylene containers and sealed hermetically where gel formation takes place.

COUNTER-EXAMPLE 1

[0052] 24.66 mL of TEOS and 2.74 mL of methyl triethoxysilane is added to 63 mL of denatured ethanol in a glass beaker and mixed for 1 minute. Consequently 11 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.0067 molar NH_4OH and 0.00333 molar NH_4F respectively) and mixed for 10 minutes. This results in water to alkoxide molar ratio of 4.89. Then, the sol is poured into polypropylene container. No gel forms at 22 °C for over 2 months and at 50 °C phase separated slurry forms that does not hold shape. By increasing the R-value the phase separation tendency increases further.

COUNTER-EXAMPLE 2

[0053] 24.66 mL of TEOS and 2.74 mL of methyl triethoxysilane is added to 30 mL of denatured ethanol in a glass beaker and mixed for 1 minute. Consequently 7.333 mL of water is added that contains HCl as catalysts (0.04 molar) and mixed for 20 minutes followed by addition of 3.666 mL of 0.08 M NaOH solution in water, further mixing for 5 min and addition of 33 mL of ethanol. This results in total water to alkoxide molar ratio of 4.89. Then, the sol is poured into polypropylene container. No gel forms at 22 °C for over 2 months and clear stable sol is obtained without noticeable increase in viscosity. Ethanol is added in two parts to increase the hydrolysis rate, otherwise dilution effect would strongly prohibit the hydrolysis to occur, evident by the exothermic nature of the reaction.

COUNTER-EXAMPLE 3

[0054] 2.222 mL of phenyltrimethoxysilane is added to 6.312 mL of denatured ethanol in a glass vial and mixed for 1 minute. Consequently 1.26 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.0067 molar NH_4OH and 0.00333 molar NH_4F respectively) and mixed for 20 minutes. This results in water to alkoxide molar ratio of 6. Opaque sol is obtained after the water is added and after 2 days at 22 °C phase separated waxy material forms at the bottom of the closed reaction vessel.

[0055] The same synthesis with R value of 4 and 0.04 M NH_4OH and 0.02 M NH_4F yields clear sol after 2 min of mixing after the water is added but in ~1.5 hours sol turns opaque and similar phase separated waxy material forms at the bottom of reaction vessel after 2 days, as compared to R value of 6.

COUNTER-EXAMPLE 4

[0056] 1.6 mL of vinyltriethoxy is added to 6.312 mL of denatured ethanol in a glass vial and mixed for 1 minute. Consequently 0.84 mL of water is added that contains NH_4OH and NH_4F as catalysts (0.04 molar NH_4OH and 0.02 molar NH_4F respectively) and mixed. This results in water to alkoxide molar ratio of 4. In 15 min clear sol is obtained but in 2 days phase separated slurry forms and no alcogel is obtained.

[0057] The counter-examples demonstrate that a gel cannot be formed with a trialkoxysilane in a composition range which is necessary to obtain an alcogel fuel tablet.

[0058] All optional and preferred features and modifications of the described embodiments and dependent claims are usable in all aspects of the invention taught herein. Furthermore, the individual features of the dependent claims, as well as all optional and preferred features and modifications of the described embodiments are combinable and interchangeable with one another.

[0059] The present application claims priority of the disclosures in UK patent application number 1913244.8.

Claims

1. A method of preparing an alcogel for use as a source of fuel, including the steps of hydrolysing at least one tetraalkoxysilane with water in the presence of a solvent and catalyst at a pH which is higher or lower than pH7, wherein the tetraalkoxysilane is tetraethoxysilane (TEOS), tetrapropoxysilane (TPOS), or any combination thereof, wherein the solvent includes ethanol, denatured ethanol, 1-propanol, 1,6-hexanediol, or any combination thereof, and wherein the molar ratio (R) of water to tetraalkoxysilane is from 5 to 7, including the step of controlling the pH of the resulting alcogel to be about 7.

2. A method as claimed in claim 1, wherein R is about 6.

3. A method as claimed in any preceding claim, wherein the ratio of solvent to tetraalkoxysilane is greater than 1:1.

4. A method as claimed in any preceding claim, wherein the ratio of solvent to tetraalkoxysilane is greater than 2:1.

5. A method as claimed in any preceding claim wherein the catalyst is an acid or base catalyst.

6. A method as claimed in claim 5, wherein the catalyst is a combination of ammonium hydroxide and ammonium fluoride.

7. A method as claimed in any preceding claim, including the additional step of storing the alcogel in a hermetically sealed container in order to minimise evaporation of said at least one alcohol.

8. A method as claimed in any preceding claim wherein the pH is controlled by the use of acid and/or base catalysts.

9. A method as claimed in any preceding claim, wherein the only reactant that is hydrolysed is a tetraalkoxysilane.

10. A fuel tablet for a camping stove including an alcogel obtainable by means of a method as claimed in any preceding claim which is contained in a hermetically sealed container.

11. A fuel tablet as claimed in claim 10, wherein the container is a paper-based wrapper or is a paraffin layer around the alcogel.

12. A method of creating heat including the step of burning an alcogel made by a method as claimed in any of claimed 1 to 9 or by removing a fuel tablet from the container of claim 10 or 11 and then burning it.

Patentansprüche

1. Verfahren zur Herstellung eines Alcogels zur Verwendung als Brennstoffquelle, umfassend die Schritte der Hydrolyse mindestens eines Tetraalkoxysilans mit Wasser in Gegenwart eines Lösungsmittels und eines Katalysators bei einem pH-Wert, der höher oder niedriger als pH 7 ist, wobei das Tetraalkoxysilan Tetraethoxysilan (TEOS), Tetrapropoxysilan (TPOS), oder eine beliebige Kombination davon ist, wobei das Lösungsmittel Ethanol, denaturiertes Ethanol, 1-Propanol, 1,6-Hexandiol oder eine beliebige Kombination davon umfasst und wobei das Molverhältnis (R) von Wasser zu Tetraalkoxysilan 5 bis 7 beträgt, einschließlich des Schritts der Steuerung des pH-Werts des Alcogels auf etwa 7.

2. Verfahren nach Anspruch 1, wobei R etwa 6 ist.

3. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Verhältnis von Lösungsmittel zu Tetraalkoxysilan größer als 1:1 ist.

4. Verfahren nach einem der vorangehenden Ansprüche, wobei das Verhältnis von Lösungsmittel zu Tetraalkoxysilan größer als 2:1 ist.

5. Verfahren nach einem der vorangehenden Ansprüche, wobei der Katalysator ein saurer oder basischer Katalysator ist.

6. Verfahren nach Anspruch 5, wobei der Katalysator eine Kombination aus Ammoniumhydroxid und Ammoniumfluorid ist.

7. Verfahren nach einem der vorhergehenden Ansprüche, einschließlich des zusätzlichen Schritts der Lagerung des Alcogels in einem hermetisch verschlossenen Behälter, um die Verdampfung des mindestens einen Alkohols zu minimieren.

8. Verfahren nach einem der vorhergehenden Ansprüche, wobei der pH-Wert durch die Verwendung von sauren und/oder basischen Katalysatoren gesteuert wird.

9. Verfahren nach einem der vorangehenden Ansprüche, wobei der einzige Reaktant, der hydrolysiert wird, ein Tetraalkoxysilan ist.

10. Brennstofftablette für einen Campingkocher, die ein Alcogel enthält, das mittels eines Verfahrens nach einem der vorhergehenden Ansprüche erhältlich ist und in einem hermetisch verschlossenen Behälter enthalten ist.

11. Brennstofftablette nach Anspruch 10, wobei der Behälter eine Umhüllung auf Papierbasis oder eine Paraffinschicht um das Alcogel ist.

12. Verfahren zur Erzeugung von Wärme, das den Schritt des Verbrennens eines Alcogels, das durch ein Verfahren nach einem der Ansprüche 1 bis 9 hergestellt wurde, oder durch Entnahme einer Brennstofftablette aus dem Behälter nach Anspruch 10 oder 11 und anschließendes Verbrennen derselben umfasst.

Revendications

1. - Procédé de préparation d'un alcogel pour une utilisation comme source de combustible, comprenant les étapes d'hydrolyse d'au moins un tétraalcoxysilane avec de l'eau en présence d'un solvant et d'un catalyseur à un pH qui est supérieur ou inférieur à pH7, dans lequel le tétraalcoxysilane est le tétraéthoxysilane (TEOS), le tétrapropoxysilane (TPOS) ou toute combinaison de ceux-ci, dans lequel le solvant comprend de l'éthanol, de l'éthanol dénaturé, du 1-propanol, du 1,6-hexanediol ou toute combinaison de ceux-ci, et dans lequel le rapport molaire (R) de l'eau au tétraalcoxysilane est de 5 à 7, comprenant l'étape de contrôle du pH de l'alcogel obtenu pour qu'il soit d'environ 7.

2. - Procédé selon la revendication 1, dans lequel R est d'environ 6.

3. - Procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport du solvant au tétraalcoxysilane est supérieur à 1:1.

4. - Procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport du solvant au tétraalcoxysilane est supérieur à 2:1.

5. - Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur est un catalyseur acide ou basique.

6. - Procédé selon la revendication 5, dans lequel le catalyseur est une combinaison d'hydroxyde d'ammonium et de fluorure d'ammonium.

7. - Procédé selon l'une quelconque des revendications précédentes, comprenant l'étape supplémentaire de stockage de l'alcogel dans un récipient hermétiquement fermé afin de rendre minimale l'évaporation dudit au moins un alcool.

8. - Procédé selon l'une quelconque des revendications précédentes, dans lequel le pH est contrôlé par l'utilisation de catalyseurs acides et/ou basiques.

9. - Procédé selon l'une quelconque des revendications précédentes, dans lequel le seul réactif qui est hydrolysé est un tétraalcoxysilane.

10. - Tablette de combustible pour un réchaud de camping comprenant un alcogel pouvant être obtenu au moyen d'un procédé selon l'une quelconque des revendications précédentes, qui est contenu dans un récipient hermétiquement fermé.

11. - Tablette de combustible selon la revendication 10, dans lequel le récipient est un emballage à base de papier ou est une couche de paraffine autour de l'alcogel.

12. - Procédé de création de chaleur comprenant l'étape consistant à brûler un alcogel obtenu par un procédé selon l'une quelconque des revendications 1 à 9 ou en retirant une tablette de combustible à partir du récipient de l'une des revendications 10 ou 11 puis en la brûlant.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 4157242 A **[0004]**
- GB 2500062 A **[0005]**
- WO 2016055814 A **[0005]**
- US 2006051627 A **[0008]**
- US 20080095928 A1 **[0009]**
- JP 2004022393 A **[0011]**
- CN 105037733 A **[0012]**
- GB 2401274 A, Barrett **[0013]**
- WO 2016055814 A1 **[0013]**
- GB 2031018 A, Twente **[0013]**
- GB 1913244 A **[0059]**