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(54) Title: HIGHLY POROUS CERAMIC OXIDE AEROGELS HAVING IMPROVED FLEXIBILITY

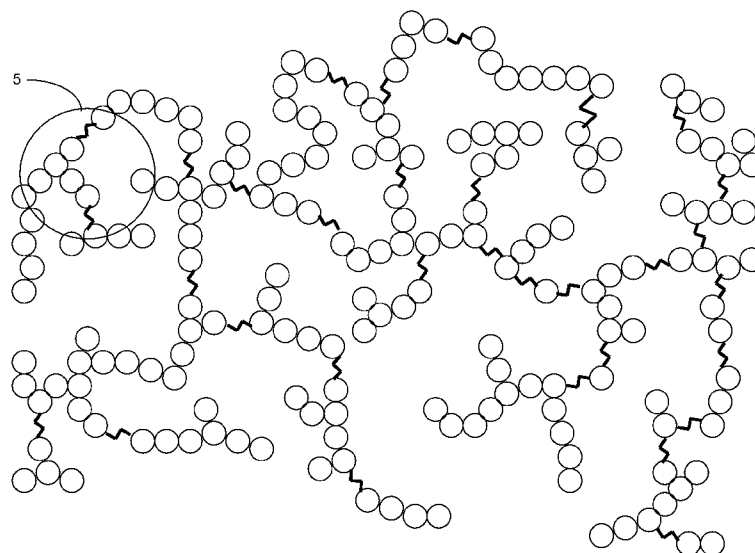


Fig. 4

(57) Abstract: Ceramic oxide aerogels incorporating periodically dispersed flexible linkages are provided. The flexible linkages impart greater flexibility than the native aerogels without those linkages, and have been shown to reduce or eliminate the need for supercritical CO₂-mediated drying of the corresponding wet gels. The gels may also be polymer cross-linked via organic polymer chains that are attached to and extend from surface-bound functional groups provided or present over the internal surfaces of a mesoporous ceramic oxide particle network via appropriate chemical reactions.

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— *with amended claims (Art. 19(1))*

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AMENDED CLAIMS

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WHAT IS CLAIMED IS:

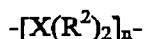
1. A ceramic-oxide network comprising interconnected strands of first particles of ceramic oxide, and a plurality of flexible linkages dispersed, but not necessarily uniformly distributed, in said network, said flexible linkages linking adjacent ones of said first particles thereby segmenting said interconnected strands,

said flexible linkages having the form



wherein:

- M is a metallic or semi-metallic element common to the ceramic oxide network; and
- L comprises a chain linkage between the opposing M atoms that has the form



wherein:

- X can be C or another atom in the chain between the opposing M atoms;
- each R² independently is any side group that will not prevent reaction(s) used to synthesize said ceramic oxide network incorporating said flexible linkage; and
- n is a positive integer equal to or lower than 10.

2. The ceramic-oxide network of claim 1, said ceramic-oxide network being a silica network wherein:

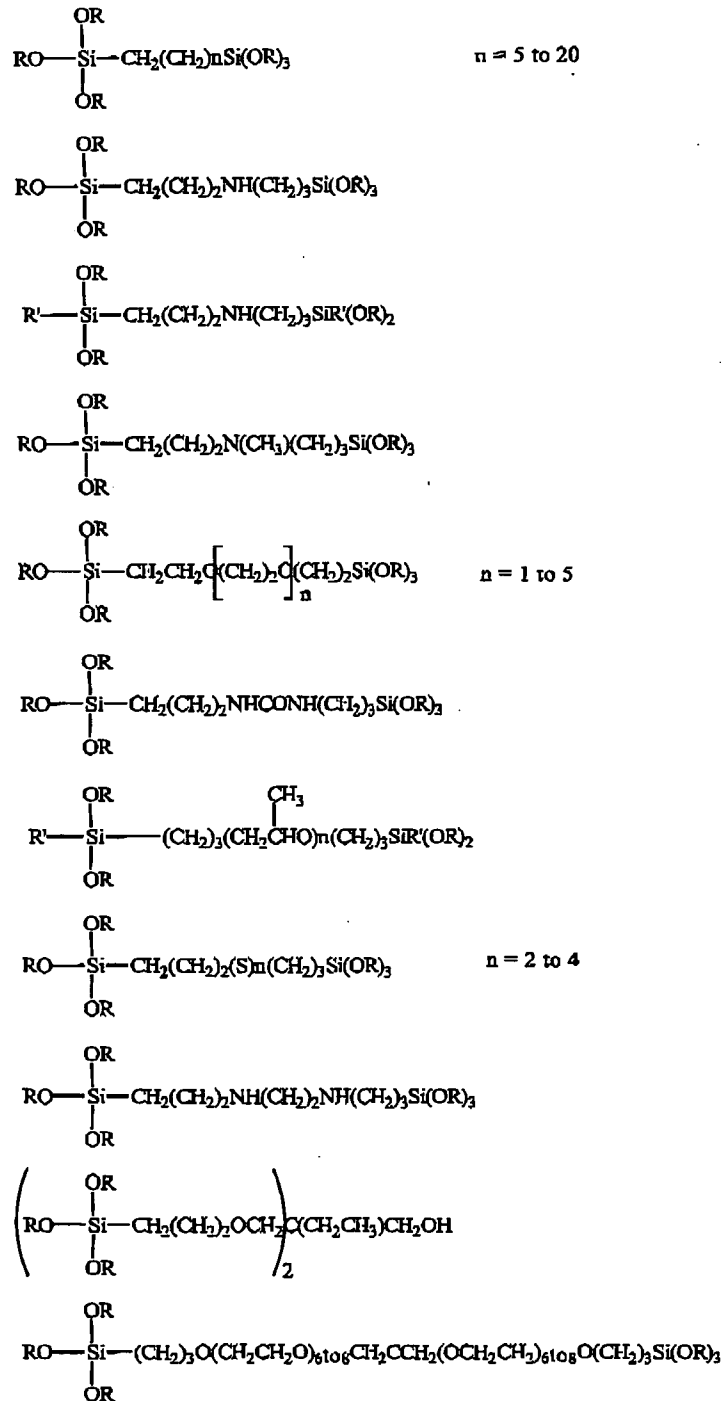
- M is Si; and
- each R² in the flexible linkage independently is H or a substituted or unsubstituted alkyl or aryl group.

3. The ceramic-oxide network of claim 2, at least one R² in said flexible linkage comprising a reaction site effective as an anchor for polymer cross-linking said network.

4. The ceramic-oxide network of claim 2, wherein at least one X atom in the $[X(R^2)_2]_n$ chain is an atom other than C.

5. The ceramic-oxide network of claim 1, said flexible linkages having the form

-Si-L-Si- and being provided from at least one flexible-linkage precursor selected from the group consisting of:



wherein each R and R' in each of the above is individually selected as hydrogen, alkyl or other moieties, and R's in each of the above are different from Rs attached to the same atom therewith, said flexible linkages being formed through hydrolysis of Si-O bonds in the selected flexible-linkage precursor(s), wherein said flexible linkages are incorporated into said network via attachment of terminal silicon atoms thereof to said first particles via Si-O-Si bonds.

6. The ceramic-oxide network of claim 1, said flexible linkages having the form -Si-L-Si- wherein L incorporates intermediate aromatic functionality.

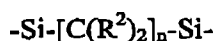
7. The ceramic-oxide network of claim 1, said first particles having an average particle size greater than 5 nm and being made up of agglomerations of relatively smaller, tightly-packed second particles of ceramic-oxide having a particle less than 2 nm, wherein said interconnected first-particle strands, segmented by said flexible linkages, define a mesoporosity of said ceramic-oxide network.

8. The ceramic-oxide network of claim 1, further comprising non-hydroxyl functional groups bound to surfaces of said first particles, said network of ceramic oxide particles being cross-linked via organic polymer chains that are attached to said first particles via reaction with at least a portion of said surface-bound non-hydroxyl functional groups.

9. The ceramic-oxide network of claim 8, said organic polymer chains being in the form of a substantially conformal polymer coating over said first-particle strands.

10. The ceramic-oxide network of claim 8, said flexible linkages comprising additional functional groups attached thereto, said organic polymer chains being further attached to said additional functional groups.

11. The ceramic-oxide network of claim 10, said ceramic-oxide network being a silica network, said flexible linkages having the form



wherein:

n is equal to or lower than 6 ; and

said additional functional groups are provided in at least a portion of said R² groups or attached to Si atoms in said flexible linkages.

12. The ceramic-oxide network of claim 8, said non-hydroxyl functional groups comprising amines.

13. The ceramic-oxide network of claim 8, said organic polymer chains comprising polyurea chains.

14. The ceramic-oxide network of claim 8, said organic polymer chains being provided via copolymerization of at least two distinct monomeric species.

15. The ceramic-oxide network of claim 8, said interconnected first-particle strands defining a mesoporosity of said ceramic-oxide network, wherein the mesoporous network has a volume void fraction of at least 80%.

16. The ceramic-oxide network of claim 15, said volume void fraction being about or at least 95%.

17. The ceramic-oxide network of claim 8, said first particles being silica particles and said surface-bound non-hydroxyl functional groups comprising groups selected from the group consisting of amines and vinyl groups.

18. The ceramic-oxide network of claim 17, said organic polymer chains being in the form of a substantially conformal polymer coating over said first-particle strands, which polymer coating is attached to said first particles via linkages with said surface-bound non-hydroxyl functional groups.

19. The ceramic-oxide network of claim 8, said non-hydroxyl functional groups being selected from the group consisting of amines and vinyl groups.

20. The ceramic-oxide network of claim 1, said network being a silica wet gel that is sufficiently flexible that it can be bent into a plurality of different conformations without breaking.

21. The ceramic-oxide network of claim 1, said network being a silica wet gel produced from a reaction mixture comprising a tetraalkylorthosilicate, 1,6-bis(trimethoxysilyl)hexane as a precursor to said flexible linkages, and water in an organic solvent, said wet gel being produced from said reaction mixture via hydrolysis and condensation reactions.

22. The ceramic-oxide network of claim 1, said flexible linkages each comprising a hexane chain.

23. A method of preparing a ceramic-oxide network, comprising copolymerizing a reaction mixture comprising at least one ceramic-oxide precursor species and at least one flexible-linkage precursor through one or a series of chemical reactions to produce said ceramic-oxide network, said at least one ceramic-oxide precursor species comprising a metallic or semimetallic element bound to at least one moiety through a bond that is labile under conditions of said one or a series of chemical reactions, said at least one flexible-linkage precursor having the form



wherein:

- M is a metallic or semi-metallic element;
- each R is attached to the associated M atom via a bond that is labile under the conditions of said reaction(s) and is individually selected to be an alkyl, alkoxy or other group that will not prevent said reaction(s);

- each R^1 is attached to the associated M atom via a bond that is not labile under the conditions of said reaction(s) and can be individually selected to be an alkyl or other group that will not prevent said reaction(s);

- L comprises a chain linkage between the opposing M atoms that has the form

$$-[X(R^2)_2]_n-$$

wherein X can be C or another atom in the chain between the opposing M atoms; each R^2 independently is any side group that will not prevent reaction(s) used to synthesize said ceramic oxide network incorporating said flexible linkage; and n is a positive integer equal to or lower than 10 ;

- x and y are both integers with y being not less than 1, wherein the sum $x + y$ is equal to the valence of M minus 1; and

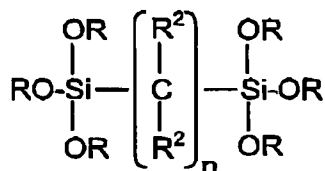
- x' and y' are both integers with y' being not less than 1, wherein the sum $x' + y'$ is equal to the valence of M minus 1.

24. The method of claim 23, said at least one ceramic-oxide precursor species comprising an unfunctionalized ceramic-oxide precursor species, wherein all moieties attached to a metallic or semi-metallic atom thereof are attached via bonds that are labile under conditions of said reaction(s).

25. The method of claim 24, said at least one ceramic-oxide precursor species further comprising a functionalized ceramic-oxide precursor species, wherein at least one moiety comprising a non-hydroxyl functional group is attached to a metallic or semi-metallic atom thereof via a bond that is not labile under conditions of said reaction(s).

26. The method of claim 23, M being a metallic or semi-metallic element common to said at least one ceramic-oxide precursor species.

27. The method of claim 23, said at least one ceramic-oxide precursor species comprising Si as the metallic or semi-metallic element, M being Si, said flexible-linkage precursor having the form:



wherein each R is as described in claim 25, and each R² is individually selected to be hydrogen or a substituted or unsubstituted alkyl or other group that will not prevent said reaction(s).

28. The method of claim 27, wherein n is equal to or lower than 6 .
29. The method of claim 23, said at least one flexible-linkage precursor comprising 1,6-bis(trimethoxysilyl)hexane.
30. The method of claim 23, further comprising providing non-hydroxyl functional groups over internal surfaces of said network, and linking at least a portion of said non-hydroxyl functional groups with an organic polymer.
31. The method of claim 30, said non-hydroxyl functional groups being selected from the group consisting of amines and vinyl groups.
32. The method of claim 31, said organic polymer comprising a polymer selected from the group consisting of polyurea, polystyrene and epoxy polymers.
33. The method of claim 30, said ceramic-oxide network being a silica network prepared through copolymerizing the following silanes:
50-100 wt.% total of a) functionalized silica precursor species selected from the group consisting of 3-aminopropyl triethylorthosilicate, vinyltrimethoxysilane and p-trimethoxysilyl-styrene, and b) bi-siloxyl-terminal flex link precursor species;
balance tetraalkylorthosilicates;
wherein all of the above weight percentages are calculated based only on the total silanes in the reaction mixture.
34. The method of claim 33, said tetraalkylorthosilicates comprising at least one of tetramethylorthosilicate and tetraethylorthosilicate.

35. The method of claim 33, said bi-siloxy-terminal flex link precursor species comprising 1,6-bis(trimethoxysilyl)hexane.

36. The method of claim 33, said network being prepared through copolymerizing 66-100 wt.% total of said functionalized silica precursor species and bi-siloxy-terminal flex link precursor species.

37. The method of claim 33, wherein a wet gel produced through copolymerizing said silanes exhibits substantial green strength prior to linking said organic polymer to said non-hydroxyl functional groups.

38. The method of claim 23, said ceramic-oxide network being an amine-decorated silica network prepared by reacting an alkoxy silane, 3-aminopropyl triethylorthosilicate and a bi-siloxy-terminal flexible-linkage precursor together under hydrolysis conditions to copolymerize them and thereby produce said silica network having amine functionality provided over internal surfaces thereof and flexible linkages dispersed throughout, but not necessarily uniformly distributed in, said network, said flexible linkages linking adjacent silica particles that are arranged in interconnected strands, thereby segmenting said interconnected strands.

39. The method of claim 23, said ceramic-oxide network being an amine-decorated silica network prepared by reacting an alkoxy silane, vinyltrimethoxysilane and a bi-siloxy-terminal flexible-linkage precursor together under hydrolysis conditions to copolymerize them and thereby produce said silica network having vinyl functionality provided over internal surfaces thereof and flexible linkages dispersed throughout, but not necessarily uniformly distributed in, said network, said flexible linkages linking adjacent silica particles that are arranged in interconnected strands, thereby segmenting said interconnected strands.

40. The method of claim 23, said at least one ceramic-oxide precursor species comprising Si as the metallic or semi-metallic element, M being Si, said flexible-linkage precursor having the form:



wherein R and L are as described in claim 23.

41. The method of claim 23, said ceramic-oxide network being formed through said reaction(s) as a wet gel having a pore structure that is saturated with a liquid solvent in which said reaction(s) was/were carried out, the method further comprising permitting said wet gel to dry through evaporation of said liquid solvent under ambient conditions to produce a dried aerogel, wherein the dried aerogel exhibits no perceptible shrinkage or pore-structure collapse compared to the wet gel.

42. The method of claim 23, said at least one flexible-linkage precursor comprising bis(trimethoxysilylpropyl)amine.

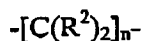
43. The ceramic-oxide network of claim 1, wherein n is equal to or lower than 6.

44. The ceramic-oxide network of claim 2, wherein n is equal to or lower than 6.

45. The ceramic-oxide network of claim 44, at least one R² in said flexible linkage comprising a reaction site effective as an anchor for polymer cross-linking said network.

46. The ceramic-oxide network of claim 44, wherein at least one X atom in the linear $[X(R^2)_2]_n$ chain is an atom other than C.

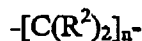
47. The method of claim 23, L having the form



wherein n is equal to or lower than 6.

48. The method of claim 27, wherein n is equal to or lower than 6.

49. The ceramic-oxide network of claim 1, L having the form



wherein n is equal to or lower than 6.

50. The ceramic-oxide network of claim 1, n being equal to or lower than 6.

51. The ceramic-oxide network of claim 1, said flexible linkages having the form -Si-(CH₂)₆-Si-.

52. The method of claim 23, said at least one flexible-linkage precursor being 1,6-bis(trialkoxysilyl)hexane.

53. The ceramic-oxide network of claim 1, said flexible linkages having the form -Si-(CH₂)₃-NH-(CH₂)₃-Si-.

54. The method of claim 23, said at least one flexible-linkage precursor being bis(trialkoxysilylpropyl)amine.

55. The ceramic-oxide network of claim 1, said flexible linkages having the form -Si-(CH₂)₃-S_n-(CH₂)₃-Si-, where n = 2 to 4.

56. (new) The method of claim 23, said at least one flexible-linkage precursor being bis(trialkoxysilylpropyl)disulfide.

57. The ceramic-oxide network of claim 1, said flexible linkages being provided from at least one flexible-linkage precursor comprising:

