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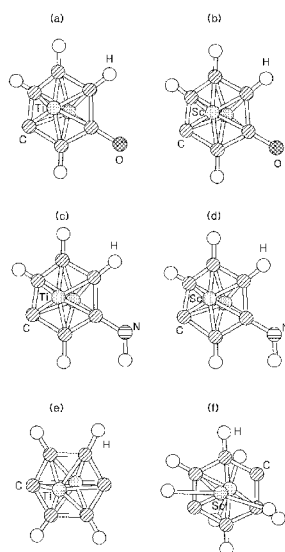
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(54) Title: HYDROGEN STORAGE MATERIALS



(57) Abstract: Disclosed herein is a hydrogen storage material, which stores hydrogen through adsorption, and, more particularly, a hydrogen storage material, which can store and use hydrogen in a state close to room temperature and atmospheric pressure and can also drastically increase hydrogen storage capacity. According to this invention, the hydrogen storage material is provided in a manner such that a light transition metal, such as titanium (Ti) or scandium (Sc), is applied on both central sites of the hexagonal structure of a polymer including polyphenol, polyaniline or polyparaphenylene, or a light transition metal, such as titanium (Ti) or scandium (Sc), is substituted for a hydrogen atom (H) of a transpoly acetylene structure, or a light transition metal, such as titanium (Ti) or scandium (Sc), is applied on both sites of a carbon chain of cis- or transpoly acetylene. Thereby, a great number of hydrogen molecules (H₂) can be adsorbed on such a metal atom to be stably stored.

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Description

HYDROGEN STORAGE MATERIALS

Technical Field

- [1] The present invention relates, generally, to a hydrogen storage material capable of storing hydrogen through adsorption, and, more particularly, to a hydrogen storage material, which can store and use hydrogen in a state close to room temperature and atmospheric pressure and can also drastically increase hydrogen storage capacity.

Background Art

- [2] In general, hydrogen is receiving attention as a clean energy source which does not discharge carbon dioxide, and thus has been thoroughly studied. To actually use hydrogen as a future energy source, techniques for producing hydrogen, for storing hydrogen, and for converting hydrogen energy into electrical energy for use in a hydrogen fuel cell must be developed. In particular, in order to replace various vehicles using gasoline or gas oil with vehicles using hydrogen energy, hydrogen storage techniques suitable for safely and conveniently storing a large amount of hydrogen to be loaded into vehicles are required.
- [3] In this regard, a variety of technologies has been developed to store hydrogen, and includes, for example, methods of compressing hydrogen at a high pressure (350 atm or 700 atm) or of cooling hydrogen to an absolute low temperature to prepare liquid hydrogen, which may then be stored. However, these methods have the drawback of entailing a safety hazard (danger of explosion). As an alternative that does not entail the safety hazard, methods of adsorbing hydrogen onto another material to store it have been devised, which are largely classified into three types as follows.
- [4] First, a method of using metal hydride is proposed, in which hydrogen is introduced into metals and is thus chemically bonded with a metal, as shown in FIG. 1a, to store hydrogen. Many scholars have studied this method during the past several decades. For example, L. Schlapbach and A. Züttel disclosed variously developed materials, including LiBH_4 , in Nature 414, 353, (2001). However, the above method is disadvantageous because a high temperature is required to separate hydrogen from the metal, due to the strong chemical bonding between metal and hydrogen. Further, the repetition of such a separation procedure may result in the deformation of the structure of the metal material, thus degrading the hydrogen storage function.
- [5] Second, a method of using a metal-organic framework is proposed. As is apparent from FIG. 1b, hydrogen may be stored between fine spaces in $\text{Zn}_4\text{O}(\text{BDC})_3$ (BDC = 1,4-benzenedicarboxylate), as disclosed in Science 300, 1127, (2003) by N.L. Rosi et al. However, the method suffers in that the maximum hydrogen storage capacity is

low, and problems similar to those encountered when using the metal hydride may occur.

- [6] Third, a method of adsorbing hydrogen onto the surface of a material having a nano-structure has been proposed. As shown in FIG. 1c, according to the content disclosed in Physical Review Letters, 94, 155504, (2005) by Y. Zhao et al, it has been noted that Sc atoms can be firmly attached onto a fullerene, and a large number of hydrogen molecules may be adsorbed onto the attached atoms. Likewise, as shown in FIG. 1d, according to the content disclosed in Physical Review Letters, 94, 175501, (2005) by T. Yildirim and S. Ciraci, it can be seen that Ti atoms can be attached onto a carbon nanotube, and a great number of hydrogen molecules may be efficiently adsorbed onto the attached atoms. Although the maximum hydrogen storage capacities of these methods are higher than those of the former methods, they are insufficient for use in automobiles. Further, since the problems of setting and arranging fullerenes and carbon nanotubes and of utilizing unnecessary inner spaces remain unsolved, the methods are difficult to apply in practice.

Disclosure of Invention

Technical Problem

- [7] Accordingly, the present invention has been made keeping in mind the above problems occurring in the related art, and an object of the present invention is to provide a hydrogen storage material, which is greatly improved to the extent that it can be actually used by satisfying standards for a hydrogen storage material required for use in automobiles by 2010 according to Department of Energy (DOE), USA, that is, at least 6% as a mass ratio of stored hydrogen relative to the total material, and at least 45 kg/m³ as a mass of hydrogen per unit volume, and also standards for hydrogen storage material required for use in automobiles by 2015, that is, at least 9% as a mass ratio of stored hydrogen relative to total material, and at least 81 kg/m³ as a mass of hydrogen per unit volume.

Technical Solution

- [8] In order to achieve the above object, the present invention provides a hydrogen storage material for storing hydrogen through adsorption, comprising a hexagonal polymer structure composed of carbons, which has a light transition metal chemically bound to both central sites of the structure.
- [9] In such a case, the polymer may be any one among polyphenol, polyaniline, and polyparaphenylene.
- [10] In addition, the present invention provides a hydrogen storage material for storing hydrogen through adsorption, comprising a hexagonal polymer structure composed of carbons, some of the carbons being substituted with boron or nitrogen, which has a

light transition metal chemically bound to both central sites of the structure.

[11] As such, the transition metal may be titanium (Ti) or scandium (Sc).

[12] In addition, the present invention provides a hydrogen storage material for storing hydrogen through adsorption, comprising a trans-polyacetylene structure, in which a light transition metal is substituted for a hydrogen atom of the structure.

[13] As such, the transition metal substituted for the hydrogen atom of the trans-polyacetylene structure may be titanium (Ti) or scandium (Sc).

[14] In this case, the Ti or Sc substituted for the hydrogen atom of the trans-polyacetylene structure may be present in the form of TiH_3 or ScH_2 due to chemical bonding with hydrogen atoms, thus realizing a structure capable of maintaining chemical stability.

[15] Further, in the hydrogen storage material, the trans-polyacetylene structure includes hydrogen atoms comprising two adjacent hydrogen atoms, each of which is replaced with TiH_3 or ScH_2 , and next two adjacent hydrogen atoms neighboring the former two adjacent hydrogen atoms, which remain unsubstituted, to provide a space where hydrogen molecules (H_2) are adsorbed, thus increasing hydrogen storage density.

[16] In addition, the present invention provides a hydrogen storage material for storing hydrogen through adsorption, comprising a cis- or trans-polyacetylene structure, in which a light transition metal is applied on both sites of a carbon chain of the structure.

[17] As such, the transition metal may be titanium (Ti) or scandium (Sc).

[18] In the case where the transition metal applied on both sites of the carbon chain of the cis-polyacetylene structure is Ti, hydrogen molecules (H_2) may be directly adsorbed on Ti. Also, in the case where the above metal is Sc, Sc may be present in the form of ScH due to chemical bonding with a hydrogen atom, such that a structure capable of maintaining chemical stability is realized and hydrogen molecules (H_2) are adsorbed on ScH .

[19] Moreover, the Ti or Sc applied on both sites of the carbon chain of the trans-polyacetylene structure may be present in the form of TiH_2 or ScH due to chemical bonding with hydrogen atoms, such that a structure capable of maintaining chemical stability is realized and a space where hydrogen molecules (H_2) are adsorbed is formed, thus increasing hydrogen storage density.

Advantageous Effects

[20] According to the present invention, the hydrogen storage material has, as a mass ratio of stored hydrogen relative to total material and a mass of hydrogen per unit volume proposed by the US DOE for application of the hydrogen storage material to automobiles by 2010, 8% and 61 kg/ m^3 respectively when titanium atoms (Ti) are attached to both central sites of the hexagonal structure of polyphenol, polyaniline or

polyparaphenylene of the material, and 8% and 61 kg/m³ respectively when scandium atoms (Sc) are attached thereto. As such, the above respective mass ratio and mass may sufficiently exceed the above proposed standards of 6% and 45 kg/m³, and thus the hydrogen storage material is able to be applied in practice because it is capable of storing hydrogen at room temperature under atmospheric pressure.

[21] Further, the hydrogen storage material has, as a mass ratio of stored hydrogen relative to total material and a mass of hydrogen per unit volume proposed by the US DOE for application of the hydrogen storage material to automobiles by 2015, 12% and 140 kg/m³ respectively, when a titanium atom (Ti) is substituted for a hydrogen atom (H) linked to a carbon chain of trans-polyacetylene of the material, and 14% and 140 kg/m³ respectively when scandium (Sc) is substituted therefor. As such, the above mass ratio and mass may sufficiently exceed the respective standards proposed above of 9% and 81 kg/m³, and thus the hydrogen storage material is able to be applied in practice.

[22] Furthermore, the hydrogen storage material is present in about 10% and about 100 kg/m³ when titanium (Ti) is applied on both sites of a carbon chain of cis- or trans-polyacetylene of the material, and 12% and about 100 kg/m³ when scandium (Sc) is applied thereon, sufficiently exceeding the above proposed standards of 9% and 81 kg/m³ required by 2015 by the US DOE. Accordingly, such a hydrogen storage material is able to be advantageously applied in practice.

Brief Description of the Drawings

[23] FIGS. 1a, 1b, 1c and 1d illustrate the chemical structures of conventional hydrogen storage material;

[24] FIGS. 2a and 2b illustrate the chemical structures of hydrogen storage material having a polyphenol structure, according to the present invention;

[25] FIGS. 2c and 2d illustrate the chemical structures of hydrogen storage material having a polyaniline structure, according to the present invention;

[26] FIGS. 2e and 2f illustrate the chemical structures of hydrogen storage material having a polyparaphenylene structure, according to the present invention;

[27] FIGS. 3a and 3b illustrate the chemical structures of the hydrogen storage material having a polyphenol structure, which has hydrogen molecules (H₂) adsorbed thereon, according to the present invention;

[28] FIGS. 3c and 3d illustrate the chemical structures of the hydrogen storage material having a polyaniline structure, which has hydrogen molecules (H₂) adsorbed thereon, according to the present invention;

[29] FIGS. 3e and 3f illustrate the chemical structures of the hydrogen storage material having a polyparaphenylene structure, which has hydrogen molecules (H₂) adsorbed thereon, according to the present invention;

- [30] FIG. 4a illustrates the chemical structure of a hydrogen storage material having a trans-polyacetylene structure including titanium substituted for hydrogen thereof, according to the present invention;
- [31] FIG. 4b illustrates the chemical structure of a hydrogen storage material having a trans-polyacetylene structure including scandium substituted for hydrogen thereof, according to the present invention;
- [32] FIG. 5a illustrates the chemical structure of the hydrogen storage material having a trans-polyacetylene structure including titanium substituted for hydrogen thereof, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention;
- [33] FIG. 5b illustrates the chemical structure of the hydrogen storage material having a trans-polyacetylene structure including scandium substituted for hydrogen thereof, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention;
- [34] FIGS. 6a and 6b illustrate the chemical structures of a hydrogen storage material having a cis-polyacetylene structure, according to the present invention;
- [35] FIGS. 6c and 6d illustrate the chemical structures of a hydrogen storage material having a trans-polyacetylene structure, according to the present invention;
- [36] FIGS. 7a and 7b illustrate the chemical structures of the hydrogen storage material having a cis-polyacetylene structure, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention; and
- [37] FIGS. 7c and 7d illustrate the chemical structures of the hydrogen storage material having a trans-polyacetylene structure, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention.

Mode for the Invention

- [38] Hereinafter, a detailed description will be given of the structure and function of a hydrogen storage material according to the preferred embodiments of the present invention, with reference to the appended drawings.
- [39] FIGS. 2a and 2b show the chemical structures of the hydrogen storage material having a polyphenol structure, according to the present invention, FIGS. 2c and 2d show the chemical structures of the hydrogen storage material having a polyaniline structure, according to the present invention, and FIGS. 2e and 2f show the chemical structures of the hydrogen storage material having a polyparaphenylene structure, according to the present invention.
- [40] FIGS. 3a and 3b show the chemical structures of the hydrogen storage material having a polyphenol structure, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention, FIGS. 3c and 3d show the chemical structures of

the hydrogen storage material having a polyaniline structure, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention, and FIGS. 3e and 3f show the chemical structures of the hydrogen storage material having a polyparaphenylene structure, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention.

[41] Although the polymer structure shown in the drawing is repeatedly arranged in one direction in practice, only a single unit structure is shown in FIGS. 2 and 3 for convenience.

[42] That is, in polyphenol $((C_6H_4O)_n)$, polyaniline $((C_6H_4NH)_n)$, or polyparaphenylene $((C_6H_4)_n)$, hydrogen (H , white circle) and oxygen (O , circle having crossed lines) or nitrogen (N , circle having horizontal lines) are linked to a hexagonal structure of carbon (C , circle having slanted lines), and a light transition metal, for example, a titanium atom (Ti , circle having dotted pattern) or a scandium atom (Sc , circle having dotted pattern) is attached to both central sites thereof.

[43] In practice, as in FIGS. 2a, 2c and 2e, there are shown stable structures in which Ti atoms are attached to both central sites of the hexagonal structure of each of polyphenol, polyaniline and polyparaphenylene. In FIGS. 3a and 3c, the number of hydrogen molecules (H_2 , two adjacent black circles) which are adsorbed around one Ti atom of the hydrogen storage material of FIGS. 2a and 2c is not more than 4. In FIG. 3e, the number of H_2 molecules to be adsorbed around one TiH_2 in the hydrogen storage material of FIG. 2e is not more than 3.

[44] As such, according to an accurate quantum-mechanical first principles calculation, average adsorption energy per H_2 molecule is found to be about 0.4 eV, which is the ideal value for storing hydrogen at about room temperature under about atmospheric pressure (1 atm).

[45] The repeated form of the above structure of FIGS. 2a, 2c and 2e is represented by $(C_6H_4O \square 2Ti)_n$, $(C_6H_4NH \square 2Ti)_n$ and $(C_6H_4 \square 2Ti)_n$. As in FIGS. 3a, 3c, and 3e, the structure, in which four H_2 are attached to one Ti in the hydrogen storage material of FIGS. 2a, 2c and 2e, is represented by $(C_6H_4O \square 2Ti \square 8H_2)_n$, $(C_6H_4NH \square 2Ti \square 8H_2)_n$ and $(C_6H_4 \square 2Ti \square 8H_2)_n$.

[46] As stated above, the average adsorption energy per H_2 molecule is about 0.49 eV in polyphenol or polyaniline and about 0.38 eV in polyparaphenylene, each value being regarded as ideal. That is, under conditions of room temperature and atmospheric pressure, the adsorbed H_2 may be removed for use.

[47] Likewise, as in FIGS. 2b, 2d, and 2f, there are shown stable structures, in which Sc atoms are attached to both central sites of the hexagonal structure of each of polyphenol, polyaniline and polyparaphenylene. In FIGS. 3b and 3d, the number of H_2 molecules to be adsorbed around one Sc atom of the hydrogen storage material of

FIGS. 2b and 2d is not more than 4. In FIG. 3f, the number of H_2 molecules to be adsorbed around one ScH_2 of the hydrogen storage material of FIG. 2f is not more than 3.

[48] In such cases, the average adsorption energy per H_2 molecule is about 0.22 eV, which is lower than the most preferable value (about 0.4 eV). Regardless, this material is also good hydrogen storage material in a predetermined pressurized state. The formulas of FIGS. 2b, 2d and 2f are represented by $(C_6H_4O)_n$, $(C_6H_4NH)_n$ and $(C_6H_4)_n$, and the formulas of FIGS. 3b, 3d, and 3f, showing the state in which hydrogen is stored, are represented by $(C_6H_4O)_n \cdot 8H_2$, $(C_6H_4NH)_n \cdot 8H_2$ and $(C_6H_4)_n \cdot 6H_2$.

[49] The hydrogen storage capability of the polymer structure is similar to that of polymer structure in which some of the carbon atoms of the hexagonal structure are replaced with boron (B) or nitrogen (N).

[50] Below, several standards required by 2010 according to the US DOE for actual use of the hydrogen storage material of the present invention are explained.

[51] First, the mass ratio of hydrogen, as the most important factor required to apply a hydrogen storage material to automobiles, is calculated.

[52] The hydrogen storage material having stored hydrogen on Ti is represented by $(C_6H_4O)_n \cdot 2Ti \cdot 8H_2$, $(C_6H_4NH)_n \cdot 2Ti \cdot 8H_2$ or $(C_6H_4)_n \cdot 2Ti \cdot 8H_2$, in which 2Ti are always attached to both central sites of the hexagonal structure of polyphenol, polyaniline or polyparaphenylene due to the strong chemical bonding, and thus function to confer structural stability. In the above formula, the portion where a hydrogen molecule is repeatedly stored and removed for use corresponds to $8H_2$. The mass ratio of stored hydrogen ($8H_2$) relative to the mass of $(C_6H_4O)_n \cdot 2Ti \cdot 8H_2$, $(C_6H_4NH)_n \cdot 2Ti \cdot 8H_2$ or $(C_6H_4)_n \cdot 2Ti \cdot 8H_2$ is calculated to be about 8%, which is higher than 6% as the minimum standard required for actual use. Likewise, in the case of Sc, the structure of $(C_6H_4O)_n$ or $(C_6H_4NH)_n$ and $(C_6H_4)_n$ stores hydrogen to form $(C_6H_4O)_n \cdot 2Sc \cdot 8H_2$ or $(C_6H_4NH)_n \cdot 2Sc \cdot 8H_2$ and $(C_6H_4)_n \cdot 2Sc \cdot 6H_2$, leading to mass ratios of stored hydrogen ($8H_2$ and $6H_2$) as high as about 8% and 6.5%.

[53] Second, whether the amount of hydrogen per unit volume, as an important factor required to load hydrogen into automobiles according to the US DOE, is 45 kg/l or more is calculated.

[54] When the end portion of $(C_6H_4O)_n$, $(C_6H_4NH)_n$ or $(C_6H_4)_n$ is attached to the surface of a hydrogen storage container, assuming that sufficient space for receiving a hydrogen molecule is maintained by a predetermined distance due to van der Waals force (or dispersion force), hydrogen mass stored per unit volume in the state of $(C_6H_4O)_n \cdot 2Ti \cdot 8H_2$, $(C_6H_4NH)_n \cdot 2Ti \cdot 8H_2$ or $(C_6H_4)_n \cdot 2Ti \cdot 8H_2$, having maximally adsorbed hydrogen molecules, is found to be about 61 kg/l, which is greater than the

minimum standard of the US DOE. Therefore, the above material may be used in practice. Likewise, $(C_6H_4O)_nSc_2$, $(C_6H_4NH)_nSc_2$ or $(C_6H_4)_nSc_2H_6$ is calculated to be similar.

[55] Third, in the case of $(C_6H_4O)_nTi$ or $(C_6H_4NH)_nTi$ and $(C_6H_4)_nTi$, the adsorption energy per H_2 molecule is 0.49 eV and 0.38 eV, which are ideal values for storing hydrogen at room temperature under atmospheric pressure. In addition, $(C_6H_4O)_nSc$, $(C_6H_4NH)_nSc$ and $(C_6H_4)_nScH_6$ have adsorption energy per H_2 molecule of 0.22 eV, which is a good value for easily storing hydrogen in a predetermined pressurized state.

[56] FIG. 4a shows the chemical structure of the hydrogen storage material having a trans-polyacetylene structure, in which titanium is substituted for hydrogen thereof, according to the present invention, and FIG. 4b shows the chemical structure of the hydrogen storage material having a trans-polyacetylene structure in which scandium is substituted for hydrogen thereof, according to the present invention. In addition, FIG. 5a shows the chemical structure of the hydrogen storage material having a trans-polyacetylene structure including titanium substituted for hydrogen thereof, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention, and FIG. 5b shows the chemical structure of the hydrogen storage material having a trans-polyacetylene structure including scandium substituted for hydrogen thereof, which has hydrogen molecules (H_2) adsorbed thereon, according to the present invention.

[57] That is, a light transition metal, for example, titanium (Ti) or scandium (Sc), is substituted for a hydrogen atom (H) linked to a carbon chain of trans-polyacetylene. Actually, as seen in FIG. 4a, since an atomic value of Ti is tetravalent, three H atoms are attached to Ti to form TiH_3 , which is then substituted for H of trans-polyacetylene, thus realizing a stable structure. Also, as seen in FIG. 5a, the number of hydrogen molecules (H_2) to be adsorbed around a unit of TiH_3 of the hydrogen storage material of FIG. 4a is not more than 5.

[58] As such, according to an accurate quantum-mechanical calculation principle, the average adsorption energy per H_2 molecule is found to be about 0.3 eV, which is slightly lower than the ideal value for storage of hydrogen at about room temperature under about atmospheric pressure (1 atm) but is still suitable for use in a predetermined pressurized state. To maximize the hydrogen storage, TiH_3 should be the most densely arranged while providing the space where the hydrogen molecule may be adsorbed. As in FIG. 4a, among hydrogen atoms of trans-polyacetylene, each of two adjacent hydrogen atoms is replaced with TiH_3 , and next two adjacent hydrogen atoms neighboring the above two adjacent hydrogen atoms remain unsubstituted to provide the space where H_2 may be adsorbed.

[59] The repeated form of the above structure is represented by $(C_4)_nTiH_3$, in which n is a large number defining the n repetitions of the same structure. The structure, in

which five H_2 are attached to one TiH_3 , as shown in FIG. 5a, is represented by $(C_4 \square 2TiH_3 \square 2H \square 10H_2)_n$.

[60] As stated above, the adsorption energy per hydrogen molecule is about 0.3 eV. As such, a statistical mechanical process is applied to remove the stored hydrogen. That is, when the temperature is increased slightly above room temperature at a given pressure (about 1 atm), the adsorbed H_2 may be removed for use. In addition, when the pressure is decreased slightly below the pressure applied to the storage material at a given temperature (about room temperature), the adsorbed H_2 may be removed for use.

[61] Likewise, as shown in FIG. 4b, since the atomic value of Sc is trivalent, two H atoms are attached to Sc to form ScH_2 , which is then substituted for the H of polyacetylene, thus realizing a stable structure. In addition, as is apparent from FIG. 5b, the number of H_2 molecules to be adsorbed around a unit of ScH_2 of the hydrogen storage material of FIG. 4b is not more than 6.

[62] In this case, the average adsorption energy per H_2 molecule is found to be about 0.2 eV, which is lower than the ideal value (0.4 eV). Regardless, this material is also good hydrogen storage material in a predetermined pressurized state. The structure of FIG. 4b is represented by $(C_4 \square 2ScH_2 \square 2H)_n$, and the structure having the stored hydrogen as in FIG. 5b is represented by $(C_4 \square 2ScH_2 \square 2H \square 12H_2)_n$.

[63] Below, several standards proposed by 2015 according to the US DOE for actual use of the hydrogen storage material of the present invention are explained.

[64] First, the mass ratio of hydrogen, which is the most important factor required for application of a hydrogen storage material to automobiles, is calculated.

[65] The hydrogen storage material having stored hydrogen on Ti is represented by $(C_4 \square 2TiH_3 \square 2H \square 10H_2)_n$, in which hydrogen atoms of $2TiH_3 \square 2H$ are always attached together due to the strong chemical bonding and thus function to confer structural stability. In the above formula, the portion where a hydrogen molecule is repeatedly stored and removed for use corresponds to $10H_2$. Thus, the mass ratio of stored hydrogen ($10H_2$) relative to $(C_4 \square 2TiH_3 \square 2H \square 10H_2)_n$ as total material is calculated to be 12%, which is higher than 9% as the minimum standard required for actual use, and also exceeds the mass ratio values of all hydrogen storage materials disclosed until now. Likewise, the structure of $(C_4 \square 2ScH_2 \square 2H)_n$ stores hydrogen to form $(C_4 \square 2ScH_2 \square 2H \square 12H_2)_n$, which has a mass ratio of stored hydrogen as high as 14%.

[66] Second, whether the amount of hydrogen per unit volume, as an important factor required for loading hydrogen into automobiles, proposed by the US DOE, is 81 kg/m³ or more is calculated.

[67] Examples of the storage material satisfying the above condition have not yet been found. As the result of calculation of energy depending on the distance between

molecules, the structures represented by $(C_4 \square 2TiH \square 2H)_n$ have weak repulsive force therebetween, and thus do not agglomerate. When the end portion of $(C_4 \square 2TiH \square 2H)_n$ is attached to the surface of a hydrogen storage container, the structure may be continuously maintained such that there is sufficient space required to receive a hydrogen molecule. Assuming that $(C_4 \square 2TiH \square 2H)_{10}$ having adsorbed hydrogens is spaced apart from another $(C_4 \square 2TiH \square 2H)_{10}$ by a predetermined distance by van der Waals force (or dispersion force), the mass of hydrogen stored per unit volume is found to be about 140 kg/m³, which is higher than the minimum standard. Therefore, the above material has excellent properties. Likewise, $(C_4 \square 2ScH \square 2H)_{12}$ is calculated to be similar.

[68] Third, as mentioned above, $(C_4 \square 2TiH \square 2H)_{10}$ has adsorption energy per H₂ molecule of 0.3 eV, which is a good value for storing hydrogen at room temperature in a predetermined pressurized state. In addition, $(C_4 \square 2ScH \square 2H)_{12}$ has adsorption energy per H₂ molecule of 0.2 eV, which is a good value for storing hydrogen in a predetermined pressurized state.

[69] FIGS. 6a and 6b show the chemical structures of the hydrogen storage material having a cis-polyacetylene structure, according to the present invention, and FIGS. 6c and 6d show the chemical structures of the hydrogen storage material having a trans-polyacetylene structure, according to the present invention. Further, FIGS. 7a and 7b show the chemical structures of the hydrogen storage material having a cis-polyacetylene structure, which has hydrogen molecules (H₂) adsorbed thereon, according to the present invention, and FIGS. 7c and 7d show the chemical structures of the hydrogen storage material having a trans-polyacetylene structure, which has hydrogen molecules (H₂) adsorbed thereon, according to the present invention.

[70] That is, a light transition metal, for example, titanium (Ti) or scandium (Sc), is chemically attached to both sites of a carbon chain of cis- or trans-polyacetylene.

[71] Actually, as seen in FIG. 6a, Ti atoms are attached to both sites of a carbon chain of cis-polyacetylene, thus forming a stable structure. Also, as seen in FIG. 7a, the number of hydrogen molecules (H₂) to be adsorbed around one Ti atom of the hydrogen storage material of FIG. 6a is not more than 5.

[72] As such, according to an accurate quantum-mechanical first-principles calculation, the average adsorption energy per H₂ molecule is found to be about 0.48 eV, which is regarded as ideal for the storage of hydrogen at about room temperature under about atmospheric pressure (1 atm). To maximize the storage of hydrogen, Ti atoms should be the most densely arranged while providing space where the hydrogen molecules may be adsorbed. Thus, the structure, in which Ti is attached to each of both sites of the carbon chain of cis-polyacetylene, is formed, the repeated form of the above structure being represented by $(C_4 H_4 \square 2Ti)_n$, in which n is a large number defining the n

repetitions of the same structure. Moreover, the structure, in which five H_2 are attached to one Ti, as shown in FIG. 7a, is represented by $(C_4H_4)_n \square 2Ti \square 10H_2$.

[73] As stated above, the adsorption energy per hydrogen molecule is about 0.48 eV. As such, a statistical mechanical process is applied to remove the stored hydrogen. That is, when the temperature is increased slightly above room temperature at a given pressure (about 1 atm), the adsorbed H_2 may be removed for use. In addition, when the pressure is decreased slightly below the pressure applied to the storage material at a given temperature (about room temperature), the adsorbed H_2 may be removed for use.

[74] Likewise, as shown in FIG. 6b, ScH is applied on each of both sites of a carbon chain of cis-polyacetylene, therefore forming a stable structure. In addition, as is apparent from FIG. 7b, the number of H_2 molecules to be adsorbed around a unit of ScH of the hydrogen storage material of FIG. 6b is not more than 5.

[75] In this case, the average adsorption energy per H_2 molecule is found to be about 0.2 eV, which is lower than the ideal value. Regardless, this material is also good hydrogen storage material in a predetermined pressurized state. The structure of FIG. 6b for maximally storing hydrogen is represented by $(C_4H_4)_n \square 2ScH$, and the structure having the maximally stored hydrogen as in FIG. 7b is represented by $(C_4H_4)_n \square 2ScH \square 10H_2$.

[76] Actually, as seen in FIG. 6c, TiH_2 is applied on each of both sites of a carbon chain of trans-polyacetylene, thus forming a stable structure. Also, as in FIG. 7c, the number of H_2 molecules to be adsorbed around a unit of TiH_2 of the hydrogen storage material of FIG. 6c is not more than 4.

[77] As such, average adsorption energy per H_2 is found to be about 0.3 eV, which is slightly lower than the ideal value but also functions as a good hydrogen storage material in a predetermined pressurized state. The structure of FIG. 6c for maximally storing hydrogen is represented by $(C_4H_4)_n \square 2TiH_2$, and the structure having the maximally stored hydrogen, as shown in FIG. 7c, is represented by $(C_4H_4)_n \square 2TiH_2 \square 8H_2$.

[78] Likewise, as seen in FIG. 6d, ScH is applied on each of both sites of a carbon chain of trans-polyacetylene, thus forming a stable structure. As well, as in FIG. 7b, the number of H_2 molecules to be adsorbed around a unit of ScH of the hydrogen storage material of FIG. 6b is not more than 5.

[79] As such, the average adsorption energy per H_2 molecule is found to be about 0.16 eV, which is lower than the ideal value but also functions as a good hydrogen storage material in a predetermined pressurized state. The structure of FIG. 6d for maximally storing hydrogen is represented by $(C_4H_4)_n \square 2ScH$, and the structure having the maximally stored hydrogen, as in FIG. 7d, is represented by $(C_4H_4)_n \square 2ScH \square 10H_2$.

[80] Below, several standards proposed by 2015 according to the US DOE for actual use

of the hydrogen storage material of the present invention are explained.

[81] First, a mass ratio of hydrogen, as the most important factor required to apply a hydrogen storage material to automobiles, is calculated.

[82] The hydrogen storage material having hydrogen adsorbed on Ti of cis-polyacetylene thereof is represented by $(C_4H_4)_n(2Ti)(10H_2)$, in which 2Ti are always attached to the both sites due to the strong chemical bonding. In the above formula, the portion where a hydrogen molecule is repeatedly stored and removed for use corresponds to $10H_2$. Therefore, a mass ratio of stored hydrogen ($10H_2$) relative to the mass of $(C_4H_4)_n(2Ti)(10H_2)$ as total material is calculated to be 10%, which is higher than 9% as a minimum standard required for actual use and also exceeds the mass ratio values of all hydrogen storage materials disclosed until now. Likewise, in the case of Sc, the structure having the stored hydrogen is represented by $(C_4H_4)_n(2ScH)(10H_2)$, which has a mass ratio of stored hydrogen as high as 12%.

[83] In addition, the hydrogen storage material having hydrogen adsorbed on Ti of trans-polyacetylene thereof is represented by $(C_4H_4)_n(2TiH)(8H_2)$, in which hydrogens to 2Ti are always attached together due to the strong chemical bonding and thus function to confer structural stability. In the above formula, the portion where a hydrogen molecule is repeatedly stored and removed for use corresponds to $8H_2$. Hence, a mass ratio of stored hydrogen ($8H_2$) relative to the mass of $(C_4H_4)_n(2TiH)(8H_2)$ as total material is calculated to be 10%, which is higher than 9% as a minimum standard required for actual use and also exceeds the mass ratio values of all hydrogen storage materials disclosed until now. Likewise, in the case of Sc, the structure having the stored hydrogen is represented by $(C_4H_4)_n(2ScH)(10H_2)$, which has a mass ratio of stored hydrogen as high as 12%.

[84] Second, whether the amount of hydrogen per unit volume, as the important factor required to load hydrogen into automobiles by 2015 according to the US DOE, is 81 kg/ℓ or more is calculated.

[85] Examples of the storage material satisfying the above condition have not yet been found. When the end portion of cis- or trans-polyacetylene is attached to the surface of a hydrogen storage container, assuming that a space sufficient for receiving a hydrogen molecule is maintained by a predetermined distance due to van der Waals force (or dispersion force), the hydrogen mass stored per unit volume of $(C_4H_4)_n(2TiH)(8H_2)$ having maximally adsorbed hydrogens, spaced apart from another $(C_4H_4)_n(2Ti)(8H_2)$, is found to be about 100 kg/ℓ, which satisfies the standard proposed by the US DOE for use in automobiles. Likewise, $(C_4H_4)_n(2ScH)(10H_2)$ is calculated to be about 100 kg/ℓ, which exceeds a minimum standard proposed by the US DOE and thus is regarded as more favorable in volume than $(C_4H_4)_n(2TiH)(8H_2)$.

[86] Third, in the case of Ti of cis-polyacetylene, the adsorption energy per H_2 molecule

in $(C_4H_4)_2TiH_8$ is measured to be 0.48 eV, which is the most ideal value able to store hydrogen at room temperature under atmospheric pressure. In the case of Sc of cis-polyacetylene, the adsorption energy per H_2 molecule in $(C_4H_4)_2ScH_{10}$ is 0.2 eV, which is a value for storing hydrogen in a predetermined pressurized state. On the other hand, in the case of Ti of trans-polyacetylene, the adsorption energy per H_2 molecule in $(C_4H_4)_2TiH_8$ is measured to be 0.30 eV, which is a relatively good value in a predetermined pressurized state under conditions of room temperature and atmospheric pressure. Further, in the case of Sc of trans-polyacetylene, the adsorption energy per H_2 molecule in $(C_4H_4)_2ScH_{10}$ is as low as 0.16 eV, but such a hydrogen material can store four H_2 molecules per Sc atom for use.

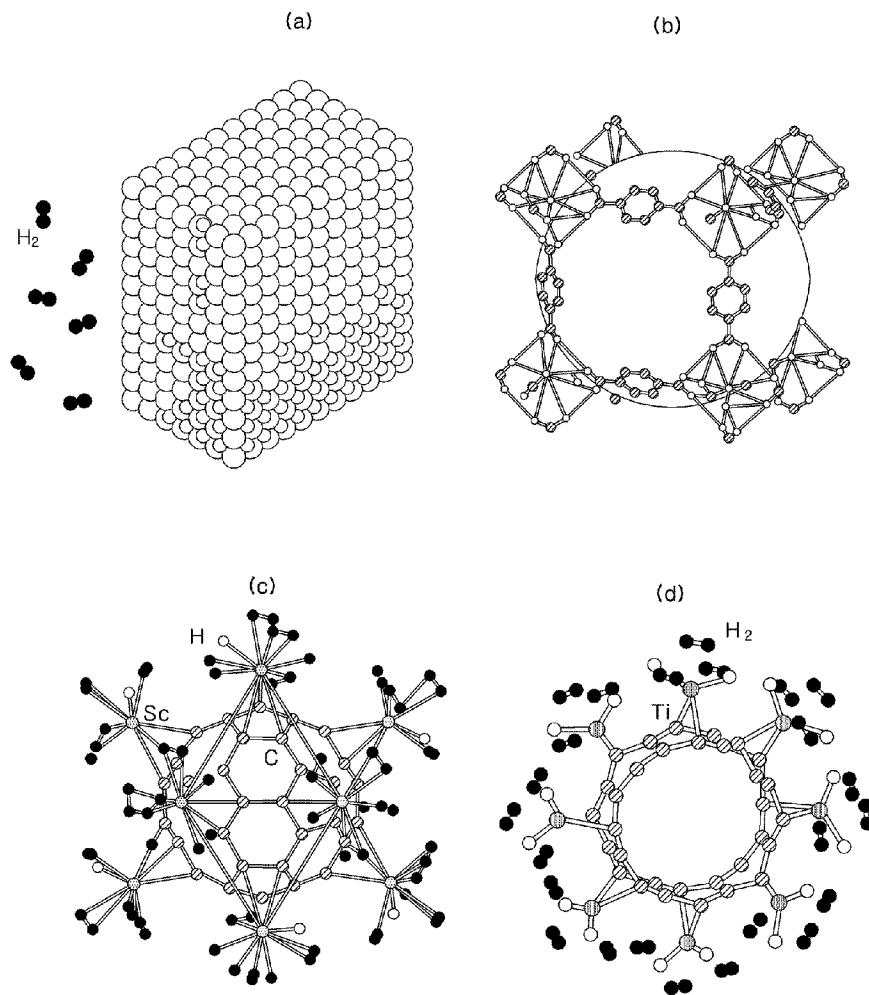
[87] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

Claims

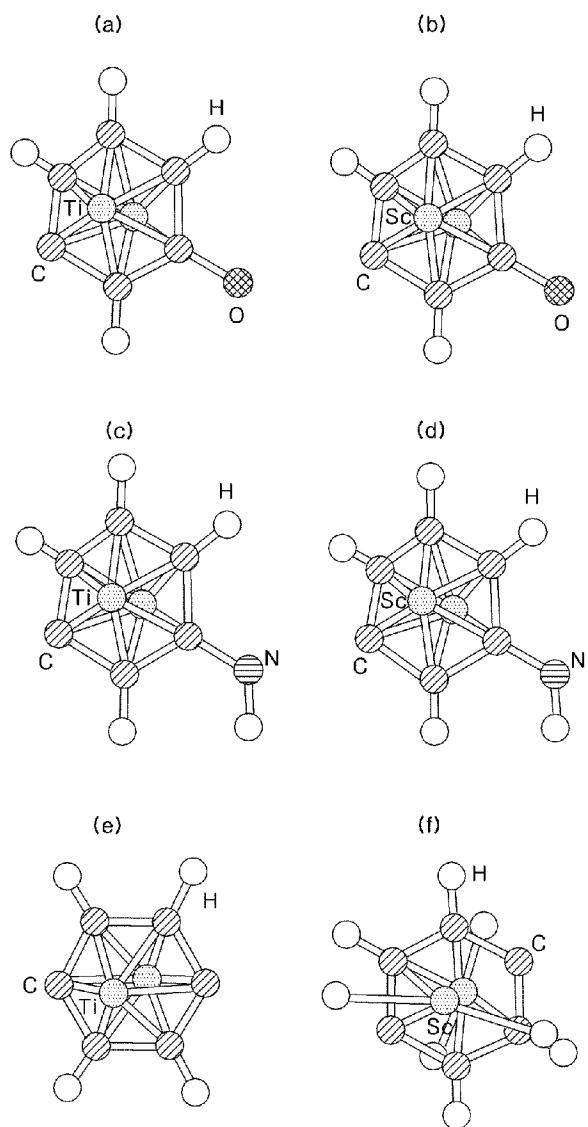
- [1] A hydrogen storage material for storing hydrogen through adsorption, comprising a hexagonal polymer structure composed of carbons, which has a light transition metal chemically bound to two central sites of the structure.
- [2] The hydrogen storage material as set forth in claim 1, wherein the polymer is any one among polyphenol, polyaniline, and polyparaphenylene.
- [3] A hydrogen storage material for storing hydrogen through adsorption, comprising a hexagonal polymer structure composed of carbons, some of the carbons being substituted with boron or nitrogen, which has a light transition metal chemically bound to two central sites of the structure.
- [4] The hydrogen storage material as set forth in any one of claims 1 to 3, wherein the transition metal is titanium (Ti) or scandium (Sc).
- [5] A hydrogen storage material for storing hydrogen through adsorption, comprising a trans-polyacetylene structure in which a light transition metal is substituted for a hydrogen atom of the structure.
- [6] The hydrogen storage material as set forth in claim 5, wherein the transition metal substituted for the hydrogen atom of the trans-polyacetylene structure is titanium (Ti) or scandium (Sc).
- [7] The hydrogen storage material as set forth in claim 6, wherein the titanium (Ti) or scandium (Sc) substituted for the hydrogen atom of the trans-polyacetylene structure is present in a form of TiH_3 or ScH_2 due to chemical bonding with hydrogen atoms, thus realizing a structure capable of maintaining chemical stability.
- [8] The hydrogen storage material as set forth in claim 6 or 7, wherein the trans-polyacetylene structure includes hydrogen atoms comprising two adjacent hydrogen atoms, each of which is replaced with TiH_3 or ScH_2 , and next two adjacent hydrogen atoms neighboring the former two adjacent hydrogen atoms, which remain unsubstituted to provide a space where hydrogen molecules (H_2) are adsorbed, thus increasing hydrogen storage density.
- [9] A hydrogen storage material for storing hydrogen through adsorption, comprising a cis-polyacetylene structure in which a light transition metal is applied on both sites of a carbon chain of the structure.
- [10] A hydrogen storage material for storing hydrogen through adsorption, comprising a trans-polyacetylene structure in which a light transition metal is applied on two sites of a carbon chain of the structure.
- [11] The hydrogen storage material as set forth in claim 9 or 10, wherein the transition metal applied on the two sites of the carbon chain of the cis- or trans-

- polyacetylene structure is titanium (Ti) or scandium (Sc).
- [12] The hydrogen storage material as set forth in claim 11, wherein, when the transition metal applied on the two sites of the carbon chain of the cis-polyacetylene structure is titanium (Ti), hydrogen molecules (H_2) are directly adsorbed on the titanium (Ti).
- [13] The hydrogen storage material as set forth in claim 11, wherein, when the transition metal applied on the two sites of the carbon chain of the cis-polyacetylene structure is scandium (Sc), the scandium (Sc) is present in a form of ScH due to chemical bonding with a hydrogen atom, such that a structure capable of maintaining chemical stability is realized and a hydrogen molecules (H_2) are adsorbed on ScH.
- [14] The hydrogen storage material as set forth in claim 11, wherein the titanium (Ti) or scandium (Sc) applied on the two sites of the carbon chain of the trans-polyacetylene structure is present in a form of TiH_2 or ScH due to chemical bonding with hydrogen atoms, such that a structure capable of maintaining chemical stability is realized and a space where hydrogen molecules (H_2) are adsorbed is provided, thus increasing hydrogen storage density.

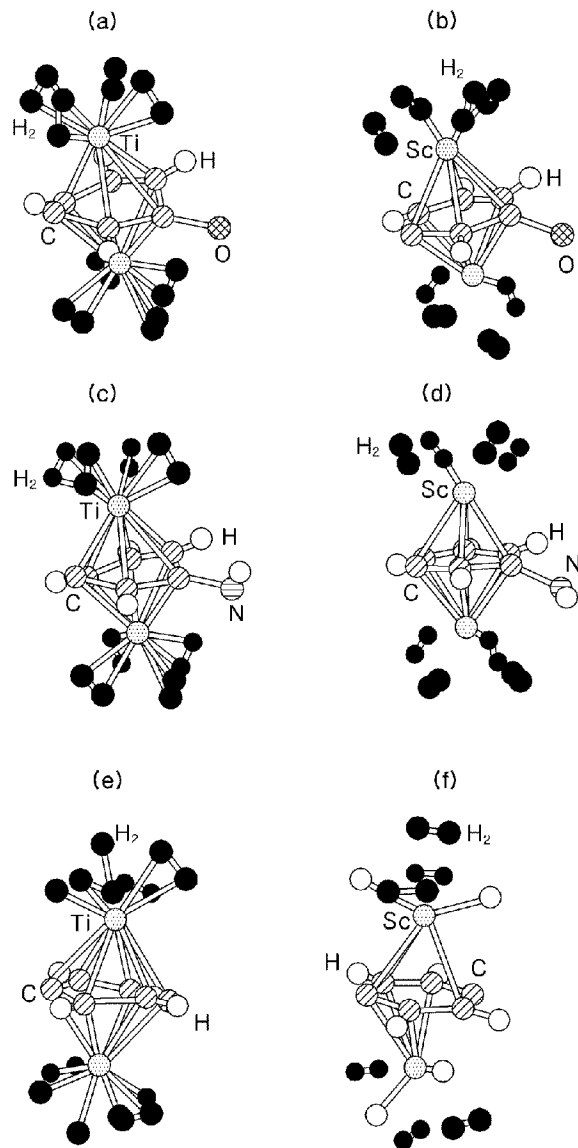
[Fig. 1]



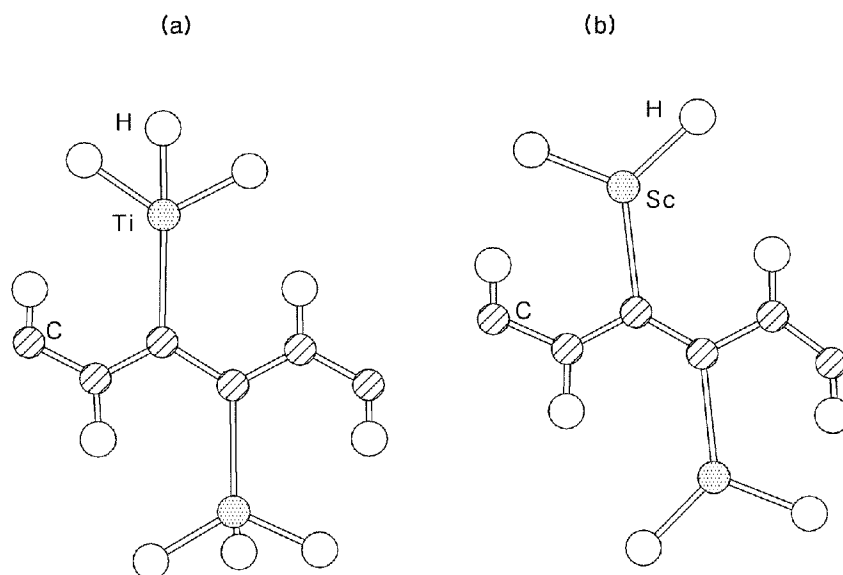
[Fig. 2]



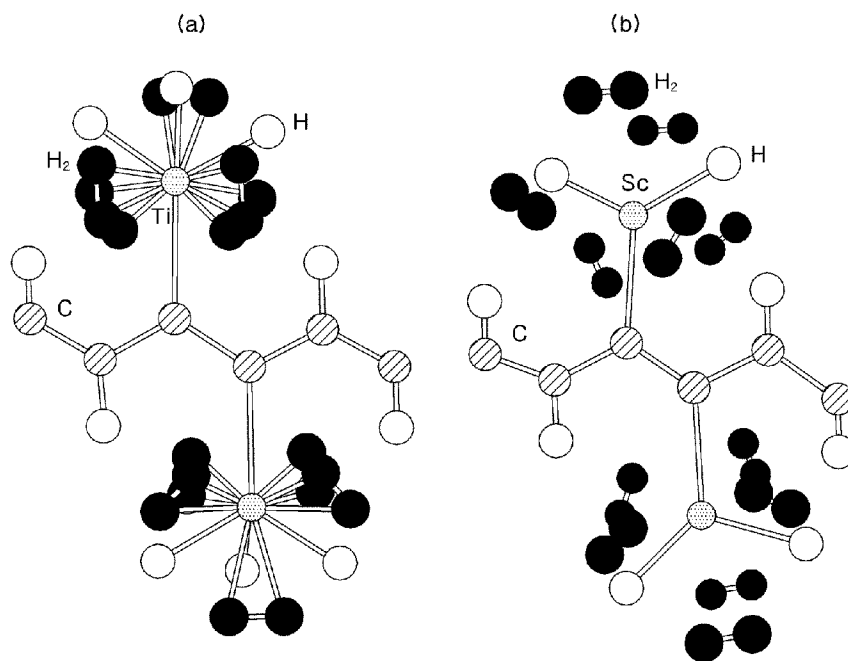
[Fig. 3]



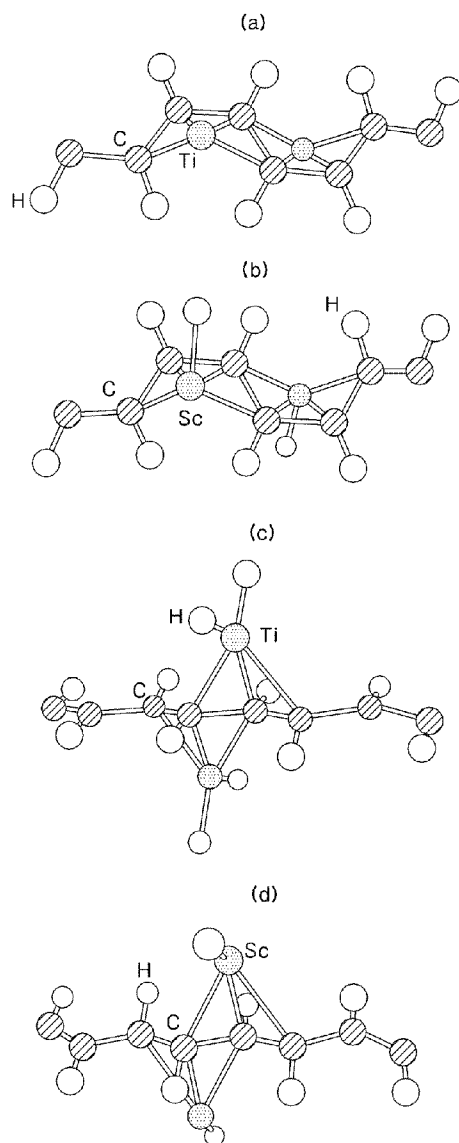
[Fig. 4]



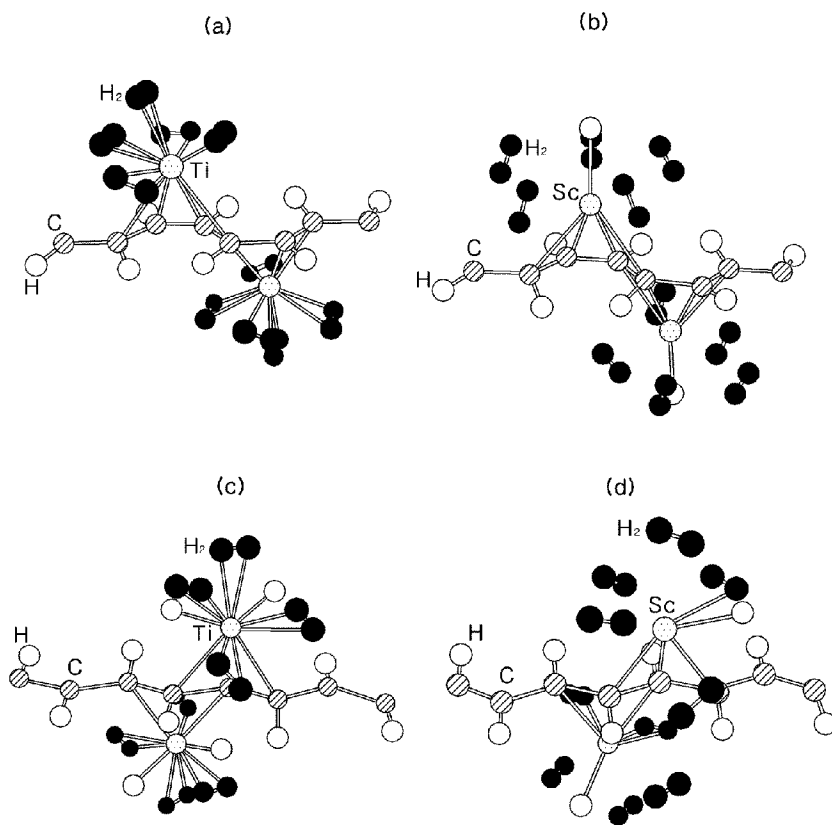
[Fig. 5]



[Fig. 6]



[Fig. 7]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2006/002641

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

- I. Claims 1 to 4 are directed to a hydrogen storage material for storing hydrogen through adsorption, comprising a hexagonal polymer structure composed of carbons, which has a light transition metal chemically bound to two central sites of the structure.
 - II. Claims 5 to 8 are directed to a hydrogen storage material for storing hydrogen through adsorption, comprising a trans-polyacetylene structure in which a light transition metal is substituted for a hydrogen atom of the structure.
 - III. Claims 9 to 14 are directed to a hydrogen storage material for storing hydrogen through adsorption, comprising a cis-polyacetylene structure or trans-polyacetylene structure in which a light transition metal is applied on both sites of a carbon chain of the structure.
1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
 2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
 3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
 4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2006/002641**A. CLASSIFICATION OF SUBJECT MATTER***C08G 83/00(2006.01)i, B01J 20/26(2006.01)i, C01B 3/00(2006.01)i*

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8: C08G, B01J, C01B, C08F

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

KOREAN PATENTS AND APPLICATIONS FOR INVENTIONS SINCE 1975

KOREAN UTILITY MODELS AND APPLICATIONS FOR UTILITY MODELS SINCE 1975

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

eKIPASS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 17082658 A (National Institute of Advanced Industrial & Technology) 31 Mar. 2005 See the abstract.	1 - 14
A	JP 16275951 A (HONDA MOTOR CO LTD) 07 Oct. 2004 See the abstract.	1 - 14
A	EP 1070538 A2 (The BOC Group, Inc.) 24 Jan. 2001 See the whole document.	1 - 14
P, A	JP 17232033 A (NIPPON STEEL CORP) 02. Sep. 2005 See the abstract.	1 - 14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 OCTOBER 2006 (25.10.2006)

Date of mailing of the international search report

25 OCTOBER 2006 (25.10.2006)

Name and mailing address of the ISA/KR

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Telephone No. 82-42-481-5540



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2006/002641

Patent document
cited in search reportPublication
datePatent family
member(s)Publication
date

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None

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07.10.2004

None

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10.12.2002

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02.09.2005

None