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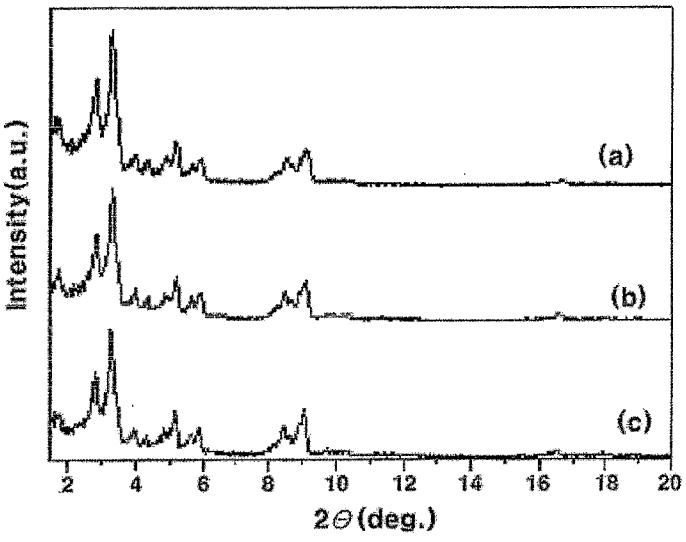
(54) Title: PREPARATION OF SURFACE FUNCTIONALIZED POROUS ORGANIC-INORGANIC HYBRID MATERIALS OR MESOPOROUS MATERIALS WITH COORDINATIVELY UNSATURATED METAL SITES AND CATALYTIC APPLICATIONS THEREOF

FIGURE 1




(57) Abstract: Disclosed herein is a method of surface-functionalization a porous organic-inorganic hybrid material, in which organic substances, inorganic substances, ionic liquids and organic-inorganic hybrid substances are selectively functionalized in coordinatively unsaturated metal sites of a porous organic-inorganic hybrid material, and thus the porous organic-inorganic hybrid material can be used for adsorbents, gas storage devices, sensors, membranes, functional thin films, catalysts, catalytic supports, and the like, and the applications of a surface functionalized porous organic-inorganic hybrid material prepared using the method to heterogeneous catalytic reactions.

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# Description

# PREPARATION OF SURFACE FUNCTIONALIZED POROUS ORGANIC-INORGANIC HYBRID MATERIALS OR MESOPOROUS MATERIALS WITH COORDINATIVELY UNSATURATED METAL SITES AND CATALYTIC APPLICATIONS THEREOF

## Technical Field

[1] The present invention relates to a nanoporous material having a large surface area, and, more particularly, to a method of selectively functionalizing organic substances, inorganic substances, ionic liquid and organic-inorganic hybrid substances in the coordinatively unsaturated metal sites of the nanoporous material, and catalytic applications of a surface functionalized nanoporous material prepared using the method.

[2] More specifically, the present invention relates to a method of surface functionalization a porous organic-inorganic hybrid material, in which organic substances, inorganic substances, ionic liquid and organic-inorganic hybrid substances are selectively functionalized in the coordinatively unsaturated metal sites (referred to as "open metal sites") of a porous organic-inorganic hybrid material (referred to as "a metal organic framework"), so that the porous organic-inorganic hybrid material can be used for adsorbents, gas storage devices, sensors, membranes, functional thin films, catalysts, catalytic supports, and the like, and to the application of a surface functionalized porous organic-inorganic hybrid material, prepared using the method, to heterogeneous catalytic reactions.

## Background Art

[3] Generally, in an organic-inorganic hybrid materials, coordinatively unsaturated metal sites can be located due to the removal of water or organic solvents, and these are the locations in which organic metal compounds can be joined by covalent or coordinate bonds.

[4] A porous organic-inorganic hybrid material, which is used in the present invention, is defined as a porous organic-inorganic polymer compound, formed by bonding an organic ligand with a central metal ion, and it is a crystalline compound which includes both organic substances and inorganic substances in its backbone structure and has a porous structure having a molecular size or a nano size. The porous organic-inorganic hybrid material, which is broadly defined, generally refers to a porous co-

ordination polymer (Angew. Chem. Intl. Ed., 43, 2334. 2004), and refers to a metal-organic framework (Chem. Soc. Rev., 32, 276, 2003). Recently, intensive and advanced research on these materials has been carried out the combination of organo-metallic compounds and the products of material science. Research into these materials has been newly advanced through the combination of the coordinate bond between molecyles and material science. Furthermore, these materials have a large surface area and molecular-sized or nano-sized pores, and can thus be used for adsorbents, gas storage devices, sensors, membranes, functional thin films, catalysts, catalytic supports, and the like. Accordingly, in recent years, research into these materials has been actively conducted.

[5] Meanwhile, since an organic-inorganic hybrid material, which is used in the present invention, has coordinatively unsaturated metal sites substituted with different metals, and possesses a regular molecular structure having a mesopore distribution in the range of 2 to 50 nm, it was reported (Chem. Rev. 97, 2373, 1997) that the organic-inorganic hybrid material can be widely applied to catalysts, catalytic supports, adsorbents and functional materials.

[6] The general surface-functionalizing methods for imparting applicability to the organic-inorganic hybrid material having a large surface area, were reported in a research paper (Curr. Opin. Solid State Mater. Sci.. 3,71, 1998, Chem. Lett. 6, 624, 2000). The method involves joining of an organic metal compound, for example, organic silane, to the surface of a previously-prepared hybrid material using a covalent bond of the organic metal compound and a hydroxide group (-OH) of the surface of the hybrid material. In addition to the method, a method of directly functionalizing the surface of a hybrid material by mixing an organic silane compound with a precursor of the hybrid material was reported in a research paper (J. Mater. Chem. 16, 1125, 2006).

[7] $\text{-Si-OH} + R_xM(OR)_{4-x}\ (1 \le x \le 3) \rightarrow \text{-Si-O-M}(OR)_{3-x}R_x + ROH$ -----(Reaction Equation 1)

[8] However, methods of selectively functionalizing the coordinatively unsaturated metal sites of the porous organic-inorganic hybrid material having few or no hydroxide groups on the surface thereof, or the coordinatively unsaturated metal sites of the organic-inorganic hybrid material substituted with different metals have not been reported yet.

[9] Recently, utilization of organic-inorganic nano hybrid materials for a number of heterogeneous catalytic reactions has been reported (J. Mater. Chem. 16, 626, 2006). But the heterogeneous catalytic reactions conducted by functionalizing the coordinatively

unsaturated metal sites of the porous organic-inorganic hybrid material have not been reported so far.

[10]

[11] Meanwhile, recently, various heterogeneous catalytic reactions using an organic-inorganic nano hybrid material have been reported in a research paper (J. Mater. Chem. 16, 626, 2006). However, examples of the heterogeneous catalytic reactions conducted by functionalizing the coordinatively unsaturated metal sites of the porous organic-inorganic hybrid material have not been reported yet.

## Disclosure of Invention

## Technical Problem

[12] The present invention has been aimed to overcome the above problems occurring in the prior art, and the object of the present invention is to provide a method of preparing a porous organic-inorganic hybrid material formed by functionalizing organic substances, inorganic substances, ionic liquid and organic-inorganic hybrid substances in the unsaturated metal sites, rather than the hydroxide groups, of the surface of the porous organic-inorganic hybrid material, and to provide applications of the porous organic-inorganic hybrid material, prepared using the method, to heterogeneous catalytic reactions.

[13] Another objective of the present invention is to provide a porous organic-inorganic hybrid prepared using the method, which can be used for adsorbents, gas storage devices, sensors, membranes, functional thin films, catalysts, catalytic supports, and the like.

[14] A further object of the present invention is to provide a catalyst composition for acid-base reaction, hydrogenation, dehydrogenation, carbon-carbon bonding reaction or oxidation reaction using the surface functionalized porous organic-inorganic hybrid material.

## Technical Solution

[15] In order to accomplish the above objectives, the present invention provides a method of preparing a surface functionalized porous organic-inorganic hybrid material by reacting a porous organic-inorganic hybrid material, having unsaturated metal sites, with one or more selected from organic substances, inorganic substances, ionic liquids and organic-inorganic hybrid substances, and provides a catalyst and composition thereof using the surface functionalized porous organic-inorganic hybrid material prepared using the method. The method is characterized in that the porous organic-

inorganic hybrid material is functionalized by selectively coordinate-bonding or covalent-bonding one or more selected from among silane, organic metal compounds and polyoxometalate to unsaturated metal sites, rather than the hydroxide group, of the surface of the porous organic-inorganic hybrid material.

[16] The porous organic-inorganic hybrid material is a porous crystalline polymer compound formed by bonding an organic ligand with a central metal ion, and the organic-inorganic hybrid material is a molecular sieve having coordinatively unsaturated metal sites substituted with different metals and ligand. The organic-inorganic hybrid material is a regular molecular sieve having a pore distribution of about 2 ~ 50 nm, and the porous organic-inorganic hybrid material generally has pores having a size of molecular scale or several nanometers.

[17] The method of the present invention may further include the step of supporting one or more metals selected from among precious metals, transition metals, and oxides thereof on the surface-functionalized porous organic-inorganic hybrid material, after the step of functionalizing the surface of the porous organic-inorganic hybrid material using one or more selected from among organic substances, inorganic substances, ionic liquids and organic-inorganic hybrid substances.

[18] Furthermore, the method of the present invention may further include the step of conducting a heterogeneous catalytic reaction using the surface-functionalized porous organic-inorganic hybrid material of the present invention.

[19] In the present invention, the porous organic-inorganic hybrid material can be prepared through a method of heating a reactant mixture solution including a metal source, an organic substance serving as a ligand, and a solvent, but is not limited thereto. The method of heating a reactant mixture solution may selectively include, but is not limited to, an electric heating method, a microwave irradiation method, an electrolytic method and a sonic wave irradiation method. However, it is preferred that the electric heating method or the microwave irradiation method be used as the method of heating a reactant mixture solution in order to prepare the crystals of a nanoporous organic-inorganic hybrid material.

[20] Any metal may be used as metals constituting the porous organic-inorganic hybrid material, and typical examples of the metals constituting the porous organic-inorganic hybrid material may include Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Mg, Ca, Sr, Ba, Sc, Y, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi and the like. In particular, transition metals that can easily form coordinate compounds can be used as the metals constituting the porous organic-

inorganic hybrid material. Among the transition metals, chromium, vanadium, iron, nickel, cobalt, copper, titanium, aluminum, manganese, and the like, and more preferably chromium, iron, aluminum and vanadium, may be used as the metals constituting the porous organic-inorganic hybrid material. In addition to the transition metals, typical elements that can form coordinate compounds may include aluminum, silicon, cerium, and lanthanum. Metals and any metal compounds may be used as the metal source.

[21] The organic substance, which is another constituent of the porous organic-inorganic hybrid material, refers to a linker. Any organic substance having coordinatively bondable functional groups may be used as the linker. Examples of the functional groups may include a carboxylic acid group, carboxylic acid anion group, amino group ($-NH_2$), imino group ($>NH$), amide group ($-CONH_2$), sulfonic acid group ($-SO_3H$), sulfonic acid anion group ($-SO_3^-$), methanedithionic acid group ($-CS_2H$), methanedithionic acid anion group ($-CS_2^-$), pyridine group, pyrazine group, and the like. In order to induce a more stable organic-inorganic hybrid material, organic substances having two or more chealating sites, such as bidentate and tridentate, can be advantageously used. The organic substances with a chealating, if they have coordinatively bondable sites, may include neutral organic substances, such as bipyridine, pyrazine and the like, anionic organic substances of carboxylic acid anion, such as terephthalate, naphthalene dicarboxylate, benzene tricarboxylate, glutarate, succinate and the like, and cationic organic substances. Carboxylic acid anions having an aromatic ring, such as terephthalate, linear carboxylic acid anions, such as formate, and anions having a non-aromatic ring, such as cyclohexyldicarbonate, may be used as the carboxylic acid anion. Organic substances having deprotonation sites and those compounds which can be changed to deprotonated form under certain reaction conditions may be used. That is, even if an organic acid, such as terephthalic acid, is used, after reaction, terephthalate can be bonded with metal components. Typical examples of the organic substances may include organic acids, such as benzene dicarboxylic acid, naphthalene dicarboxylic acid, benzene tricarboxylic acid, naphthalene tricarboxylic acid, pyridine dicarboxylic acid, bipyridyl dicarboxylic acid, formic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, hexanedioic acid, heptanedioic acid, cyclohexyl dicarboxylic acid, and anions thereof; pyridine; and pyrazine. Further, mixtures of two or more organic substances may used.

[22] In the preparation of the organic-inorganic hybrid material, suitable solvents are required. Example of the solvents may include water; alcohols, such as methanol, ethanol, propanol and the like; ketones, such as acetone, methylethyl ketone and the like; hydrocarbons, such as hexane, heptane, octane and the like; and ionic liquids. Mixtures of two or more solvents may be used, but water is the most suitable solvent.

[23] Typical examples of the porous organic-inorganic hybrid material may include chromium terephthalate, vanadium terephthalate, iron terephthalate, and aluminum terephthalate. Among them, porous organic-inorganic hybrid materials having macropores, such as MIL-100 (Angew. Chem. Int. Ed. 43, 6296, 2004), MIL-101 (Science, 309, 2040, 2005) and MOF-500 (Angew. Chem. Int. Ed. 45, 2528, 2006), are most suitable.

[24] The porous organic-inorganic hybrid material may have a thin film structure or a membrane structure. The porous organic-inorganic hybrid material having a thin film structure or a membrane structure can be prepared by immersing a substrate surface-treated with alumina, silicon, glass, indium-tin oxide (ITO), indium-zinc oxide (IZO), or a heat-resistant polymer into a reactant mixture solution.

[25] Further, examples of the organic-inorganic hybrid material having coordinatively unsaturated metal sites may include MCM-41, SBA-15, and MSU-H materials which are substituted with different metals such as B, Al, In, Ga etc. and having a hexagonal pore system, and SBA-16, SBA-1, and FDU-1, MCM-48 with a three-dimensional cubic pore system.

[26] Further, compounds which can be bonded to coordinatively unsaturated metal sites may be the one or more selected from among organic substances, inorganic substances, ionic liquids, and organic-inorganic hybrid substances. The organic compound may be one or more selected from among the compounds represented by Formulas 1 and 3 below:

[27] [Formula 1]

[28] $H_2N$-M-R1

[29] [Formula 2]

[30] HS-M-R2

[31] [Formula 3]

[32] $(OH)_2OP$-M-R3

[33] wherein M is an alkylene or aralkylene group of $C_1$~$C_{20}$ including unsaturated hydrocarbons or including no unsaturated hydrocarbons, and each of R1 and R2 is independently an organic alkylene or aralkylene group, unsubstituted or substituted with

one or more selected from among halogen elements, a vinyl group (-C=$CH_2$), an amino group (-$NH_2$), an imino group (-$NHR^{14}$), a mercapto group (-SH), a hydroxyl group (-OH), a carboxylic acid group (-COOH), a sulfonic acid group (-$SO_3H$), an alkoxy group (-OR) and a phosphoric group (-PO(OH)$_2$).

[34] Further, as the inorganic substance functionalizing materials, polyoxometallate of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ or $[PW_{12}O_{40}]^{4-}$ may be used. The polyoxometallate may include a Keggin structure anion $[(XM_{12}O_{40})^{n-}$, where n is an integer of 1 ~ 10; X is P, Si, H, Ga, Ge, V, Cr, Me or Fe; and M is one or more selected from among W, Mo, and Co], a Lindqvist structure anion $[(M_6O_{19})_{n-}$, where n is an integer of 1 ~ 10; and M is W, Mo, Ta, V or W], an Anderson-Evans structure anion $[(M_x(OH)_6M_6O_{18})^{n-}$, where n is an integer of 1 ~ 10; Mx is Cr, Ni, Fe, or Mn; and M is Mo, or W] or $[(M_4(H_2O)_4(P_2W_{15}O_{56})_2)^{n-}$, where n is an integer of 1 ~ 10; and M is one or more transition metals or transition metal clusters selected from among Cu, Zn, Ni, Mn, and the like], and Dawson-Wells structure $(P_2W_{15}O_{56})_2$.

[35] The ionic liquids may be one or more salts selected from among ammonium, phosphonium, sulphonium, pyrrolidinium, imidazolium, thiazolium, pyridium and triazolium. Further, the organic-inorganic hybrid substances may be organic metal compounds. Among the organic metal compounds, compounds containing organic silicon may be chiefly used as organic silane compounds. Specific examples of the organic silane compounds may include silylating agents, silane coupling agents, silane polymers, and mixtures thereof.

[36] Among the surface functionalizing materials, organic silane compounds can be easily bonded to the coordinatively unsaturated metal sites of the porous organic-inorganic hybrid material and are stable after bonding. Among the organic silane compounds, an organic silane compound, having an alkoxy group at one side thereof and having an alkyl group, an alkenyl group and an alkynyl group having a functional group selected from an amino group and a mercapto group at the other side, can have stabel bonds with the porous organic-inorganic hybrid material and has high catalytic activity.

[37] Further, the organic-inorganic hybrid material is one or more selected from among compounds represented by Formulas 4 to 11 below:

[38] [Formula 4]

[39] $Si(OR^1)_{4-x}R_x$ $(1 \le x \le 3)$

[40] [Formula 5]

[41] $Si(OR^3)_{4-(y+z)}R^2_yZ_z$ $(1 \le y+z \le 3)$

[42] [Formula 6]

[43] $Si(OR^4)_{4-a}R^5_aSi$ ($1 \leq a \leq 3$)

[44] [Formula 7]

[45] $Z^1_b(OR^6)_{3-b}Si\text{-}A\text{-}Si(OR^7)_{3-C}Z^2_C$ ($0 \leq b \leq 2$, $0 \leq c \leq 2$)

[46] [Formula 8]

[47] $R^8_eM^1(OR^9)_{4-e}$ ($1 \leq e \leq 3$)

[48] [Formula 9]

[49] $R^{10}_gM^2Z^3_f(OR^{11})_{4-(f+g)}$ ($1 \leq f+g \leq 3$)

[50] [Formula 10]

[51] $M^3(OR^{12})_h$ ($1 \leq h \leq 2$)

[52] [Formula 11]

[53] $M^4(OR^{13})_iZ^4_j$ ($1 \leq i+j \leq 2$)

[54] wherein A is an alkylene or aralkylene group of $C_1$~$C_{20}$ including unsaturated hydrocarbons or not including unsaturated hydrocarbons, each of $Z^1$, $Z^2$, $Z^3$ and $Z^4$ is independently selected from among halogen elements, each of $M^1$ and $M^2$ is independently one or more elements selected from among transition metals, Lanthanides and Actinides, each of $M^3$ and $M^4$ is independently one or more elements selected from among alkali metals and alkaline earth metals, each R and $R^1$ to $R^{13}$ is independently an alkyl group, alkenyl group or alkynyl group of $C_1$~$C_{20}$, unsubstituted or substituted with one or more selected from among halogen elements, a vinyl group (-C=$CH_2$), an amino group (-$NH_2$), an imino group (-NH$R^{14}$), a mercapto group (-SH), a hydroxyl group (-OH), and a carboxylic acid group (-COOH), or is selected from among a vinyl group (-C=CH), an amino group (-$NH_2$), an imino group (-NH$R^{14}$), a mercapto group (-SH), a hydroxyl group (-OH) and a carboxylic acid group (COOH), and $R^{14}$ is an alkyl group, an alkenyl group or an alkynyl group of $C_1$~$C_{10}$, unsubstituted or substituted with halogen, an amino group, a mercapto group or a hydroxyl group.

[55] When the porous organic-inorganic hybrid material is functionalized using one or more selected from among organic substances, inorganic substances, ionic liquids and organic-inorganic hybrid substances, the porous organic-inorganic hybrid material may be functionalized using mixtures thereof, and may be sequentially functionalized using other substances after the use of one of the substances. Preferably, the porous organic-inorganic hybrid material material is first reacted with organic substances or organic metal compounds, and subsequently in the second step reacted with ionic liquids or inorganic polyoxometallates, thereby preparing a surface functionalized porous organic-inorganic hybrid material. This method is advantageous in that the dissolution of metals can be prevented when functional groups are second supported with the

metals, which are active materials.

[56] Before the surface functionalization of the porous organic-inorganic hybrid, a pretreatment process of removing water or a solvent bonded to the coordinatively unsaturated metal sites thereof may be performed. In the pretreatment process, any method may be used as long as water or a solvent can be removed without causing the deformation of the surface functionalization of the porous organic-inorganic hybrid material. More specifically, the porous organic-inorganic hybrid material may be heated at a temperature of 100℃ or more for 2 hours, particularly at a temperature of 150℃ or more for 4 hours, under reduced pressure.

[57] A method of preparing a surface functionalized porous organic-inorganic hybrid material according to an embodiment of the present invention may include the steps of (a) removing an organic solvent, such as water (H2O), alcohol or the like, coordinatively bonded to the coordinatively unsaturated metal sites of the surface of the porous organic-inorganic hybrid material substituted with different metals; (b) functionalizing the pretreated porous organic-inorganic hybrid material by putting it in a solution formed by dissolving organic substances, inorganic substances, ionic liquids and organic-inorganic hybrid substances in a solvent and then refluxing the mixed solution; and (c) refining the porous organic-inorganic hybrid material functionalized with the organic metal compounds.

[58] When the porous organic-inorganic hybrid material is surface-functionalized using high volatile organic substances, silane or an organic metal compound, gaseous silane or an organic metal compound comes into contact with the porous organic-inorganic hybrid material, thus selectively bonding it to the coordinatively unsaturated metal sites of the porous organic-inorganic hybrid material.

[59] In the method of preparing a surface functionalized porous organic-inorganic hybrid material according to the present invention, in order to realize the applications for heterogeneous catalysts, sensors and the like, the porous organic-inorganic hybrid material surface-functionalized with organic groups, silane, organic metal compounds, ionic liquids or polyoxometallates may be supported with one or more selected from among precious metals, transition metals, typical metals, Lanthanide, or oxides thereof, and thus may be fixed. The precious metals may include single metals, such as Pd, Au, Pt, Ru, and the like, and composite metals. The transition metals may include Ti, Zr, V, Fe, Ni, Nb, W, Mo, Ta, Mn, and the like. The method of fixing the porous organic-inorganic hybrid material by supporting it with one or more selected from among precious metals, transition metals, typical metals, Lanthanide, or oxides thereof

may be conducted using general methods. In the method of fixing the porous organic-inorganic hybrid material, compounds including precious metals, transition metals, typical metals or lanthanide are reduced in a solution using a reductant and then supported, or the compound may be directly supported. Further, the compounds may be supported in the form of metal oxides.

[60] The present invention provides a surface-functionalized porous organic-inorganic hybrid material prepared using the method. Further, the present invention provides a catalyst composition including the surface functionalized porous organic-inorganic hybrid material prepared using the method. In this case, the catalyst composition may be used for an acid-base reaction, hydrogenation, dehydrogenation, carbon-carbon bonding reaction, or oxidation reaction by oxygen, air or hydrogen peroxide.

[61] The catalyst composition for hydrogenation, dehydrogenation or carbon-carbon bonding or the catalyst composition for oxidation may be first surface-functionalized using the surface-functionalized porous organic-inorganic hybrid material supported with organic groups, silane, organic metal compounds, ionic liquids or polyoxo-metallates, and may be second surface-functionalized using the surface-functionalized porous organic-inorganic hybrid material supported with one or more selected from among precious metals, transition metals or metal oxides thereof.

[62] The catalyst composition according to the present invention is a composition containing the surface-functionalized porous organic-inorganic hybrid material prepared using the methods. In the catalyst composition, the surface-functionalized porous organic-inorganic hybrid material may be independently used, and may be used by mixing other catalyst components with the catalyst composition. Further, the catalyst composition may be prepared by mixing the surface-functionalized porous organic-inorganic hybrid material with a substrate material, and may be prepared by coating a substrate with the surface-functionalized porous organic-inorganic hybrid material.

## Advantageous Effects

[63] As described above, according to the present invention, it can be seen that, since the coordinatively unsaturated metal sites of a porous organic-inorganic hybrid material are surface-functionalized, the surface of the hybrid material, having few or no hydroxy groups, can be functionalized with organic functional groups, inorganic functional groups, or organic-inorganic hybrid functional groups. Further, it can be seen that the method of functionalizing the porous organic-inorganic hybrid material according to the present invention is advantageous in that it is very rapid in the view of

kinetics and has high selectivity, compared to conventional methods of functionalizing the hydroxy groups of the surface of porous materials with organic-inorganic compounds.

[64] This surface-functionalized porous organic-inorganic hybrid material can be used to manufacture various catalysts, catalytic supports, adsorbents, gas storage devices, ion-exchange reactors, nanoreactors, and nanomaterials. In particular, this surface-functionalized porous organic-inorganic hybrid material can be used for electronic materials, chiral catalysts, sensors, photoelectric materials, and medical materials in the future.

## Brief Description of the Drawings

[65] FIG. 1 is a graph showing XRD patterns of a surface-functionalized porous organic-inorganic hybrid material, in which (a) shows the XRD pattern of MIL-101 prepared inExample 1, (b) shows the XRD pattern of DE-MIL-101 of Example 1, and (c) shows the XRD pattern of DETA-MIL-101 of Example 2;

[66] FIG. 2 is a graph showing nitrogen adsorption isotherms of a surface-functionalized porous organic-inorganic hybrid material, in which a) shows the nitrogen adsorption isotherm of MIL-101 prepared inExample 1, (b) shows the nitrogen adsorption isotherm of DE-MIL-101 of Example 1, and (c) shows the nitrogen adsorption isotherm of DETA-MIL-101 of Example 2;

[67] FIG. 3 is a graph showing infrared spectra of a surface-functionalized porous organic-inorganic hybrid material, in which a) shows the infrared spectrum of MIL-101 of Preparation Example 1, and (b) shows the infrared spectrum of DE-MIL-101 of Example 1;

[68] FIG. 4 is a TEM photograph showing a surface-functionalized porous organic-inorganic hybrid material (Pd-EDTA-MIL-101) prepared in Example 5; and

[69] FIG. 5 is a graph showing the results of EDX element analysis of the surface-functionalized porous organic-inorganic hybrid material (Pd-EDTA-MIL-101) prepared in Example 5.

[70]

## Mode for the Invention

[71] Hereinafter, the present invention will be described in more detail with reference to Examples.

[72] <Preparation Example 1> Preparation of porous organic-inorganic hybrid material (MIL-101)

[73] In Preparation Example 1, a porous organic-inorganic hybrid material (MIL-101) having a pore size of 1 nm or more was prepared (Science, 309, 2040, 2005).

[74] Reactant mixtures with the molar composition for Cr:HF:BDCA:$H_2O$= 1:1:1:275 were prepared from $Cr(NO_3)_3.9H_2O$, aques HF, 1,4-benzenedicarboxylic acid (BDCA) and water. The reacatant mixtures were loaded in Teflon reactor, Subsequently, the reactant mixture was heated in an oven at a temperature of 220℃ for 8 hours to react, was cooled to room temperature, was separated using a centrifugal separator, was cleaned using distilled water, and was then dried at a temperature of 110℃, thereby obtaining the porous organic-inorganic hybrid material (MIL-101). The X-ray diffraction patterns (XRD patterns) of solids corresponded to those of the reported research (Science 2005, 309, 2040). The XRD pattern and oxygen adsorption isotherm of the obtained porous organic-inorganic hybrid material crystal are shown in (a) of FIG. 1 and (a) of FIG. 2, respectively.

[75] <Preparation Example 2> APS-SBA-15 functionalized with amino group and base catalytic reaction

[76] SBA-15, which is a hexagonal silica mesoporous material, was prepared using a commonly known method, described in the document "J. Phys. Chem. 106, 255, 2002". It was found that the XRD pattern of the baked SBA-15 was identical to that reported in the document. In Preparation Example 2, a porous material functionalized with an amino group (APS-SBA-15) was prepared as in Example 1, except that SBA-15, which is a mesoporous material, rather than an organic-inorganic hybrid material, was used as a support for functionalization. As the result of a Knoevenagel condensation reaction, APS-SBA-15 was found to exhibit lower catalytic reactivity than $NH_2$-MIL-101 in the same reaction time. The reason for this is that -$NH_2$ group of $NH_2$-MIL-101 was more activated than APS-SBA-15 (refer to Table 1).

[77] <Example 1> ED-MIL-101 functionalized with amino group

[78] 1g of MIL-101, prepared in Preparation Example 1, was pretreated in a vacuum oven at a temperature of 200℃ for 12 hours to remove water coordinatively bonded to the coordinatively unsaturated metal sites thereof. Subsequently, 1g of the dewatered MIL-101 was put in a mixed solution of 2 ml of ethylenediamine (ED) and 48 ml of toluene. Subsequently, the mixed solution was refluxed at a temperature of 110℃ for 12 hours, separated using a paper filter, and then dried in an oven at a temperature of 110℃, thereby preparing a porous organic-inorganic hybrid material in which an amino group is coordinatively bonded to the coordinatively unsaturated metal sites thereof. From the X-ray diffraction pattern before/after the porous organic-inorganic hybrid material

was supported with ethylenediamine, it could be seen that a material having the same structure as pure MIL-101 was obtained, as shown in (b) of FIG. 1. Further, from the result of nitrogen adsorption, it could be seen that the amount of adsorbed nitrogen was decreased, as shown in (b) of FIG. 2. Further, the fact that ethylenediamine was coordinated can be seen by confirming the fact that the amino group (-$NH_2$) and ethyl group (-$CH_2CH_2$-) of the ethylenediamine were present in the frequency range of 2800~3000 $cm^{-1}$ and in the frequency range of 3200 ~ 3400 $cm^{-1}$, as shown in FIG. 3. Further, from the fact that the hydroxyl group (-OH group) of the porous organic-inorganic hybrid material before/after the coordination of ethylenediamine was changed little in the frequency range of 3550 ~ 3650$cm^{-1}$, as shown in (a) of FIG. 3, it can be seen that the ethylenediamine was selectively bonded to the coordinatively unsaturated metal sites of the porous organic-inorganic hybrid material, as shown in (b) of FIG. 3

[79] <Example 2> DETA-MIL-101 functionalized with triamino group

[80] In Example 2, MIL-101 prepared in Preparation Example 1 was used, and diethylenetriamine was used as a precursor of amino group instead of ethylenediamine used in Example. As in Example 1, 1g of MIL-101, prepared in Preparation Example 1, was pretreated in a vacuum oven at a temperature of 200℃ for 12 hours, and was then put in a mixed solution of 3.8 ml of diethylenetriamine (DETA) and 50 ml of toluene. Subsequently, the mixed solution was refluxed at a temperature of 110℃ for 12 hours, separated using a paper filter, and then dried in an oven at a temperature of 110℃, thereby preparing a porous organic-inorganic hybrid material (DETA-MIL-101) in which an amino group is coordinatively bonded to the coordinatively unsaturated metal sites thereof. It was found that the amino group (-$NH_2$) and ethylene group of the diethylenetriamine were present in DETA-MIL-101 using infrared spectroscopy, as shown in (c) of FIG. 1 and (c) of FIG. 2.

[81] <Example 3> Preparation of HS-MIL-101 having thiol group

[82] An organic-inorganic nanoporous material was functionalized with 1,2-dimercaptoethane using the same method as in Example 1, except that the 1,2-dimercaptoethane was used as a functional group for surface functionalization. It was determined that the ethylene group and thiol group (-SH) were present using infrared spectroscopy.

[83] <Example 4> Preparation of AMS-MIL-101 having both amino group and sulfonic acid group

[84] 0.5 g of MIL-101 prepared in Preparation Example 1 was pretreated in a vacuum

oven at a temperature of 200°C for 12 hours, and was then put in a mixed solution of 0.18 g of aminomethanesulfonic acid (AMS) and 50 ml of toluene. Subsequently, the mixed solution was refluxed at a temperature of 110°C for 12 hours while introducing nitrogen thereinto, thereby preparing an AMS-MIL-101 in which amino groups are bonded to the coordinatively unsaturated metal sites thereof and sulfonic acid is functionalized. It was found that the amino group (-$NH_2$) was present in the frequency range of 3200-3400 $cm^{-1}$ and that the S=O symmetric bond was present in the frequency range of 1150 $cm^{-1}$.

[85] <Example 5> Preparation of Pd-DETA-MIL-101 supported with palladium

[86] 1g of DETA-MIL-101, prepared in Example 2, was vacuum-pretreated at a temperature of 150°C, and was then dispersed in a mixed solution of 0.016 g of PdCl2 and 30 ml of ethanol to support the organic-inorganic hybrid material (DETA-MIL-101) with 1 wt% of palladium (Pd). Subsequently, 0.9 g of NaBH4, which is a reductant, was added to the mixed solution, thereby preparing a Pd-DETA-MIL-101 supported with palladium. As the result of XRD analysis, it was found that the crystal structure of the Pd-DETA-MIL-101 was maintained even if the NaBH4, which is a strong reductant, was used, as shown in FIG. 4. Further, it was found that palladium particles were distributed in the pores of MIL-101 through TEM/EDX analysis, as shown in FIG. 5.

[87] <Example 6> Preparation of Au-DETA-MIL-101 supported with gold

[88] An Au-DETA-MIL-101 supported with gold was prepared using the same method as in Example 4, except that HAuCl4 was used instead of $PdCl_2$. As the result of XRD analysis, it was found that the crystal structure of the Au-DETA-MIL-101 was maintained even if the $NaBH_4$, which is a strong reductant, was used.

[89] <Example 7> Preparation of PWA-NH2-MIL-101 supported with heteropoly anion

[90] 0.5 g of ED-MIL-101 prepared in Example 1 was mixed with PWA(10ml of 0.01M $H_3PW_{12}O_{40}\cdot 12H_2O$, MWPW = 2882), and was then stirred at room temperature for 12 hours, thereby preparing an organic-inorganic hybrid material (PWA-$NH_2$-MIL-101) supported with a heteropoly anion via the ionic bond of the heteropoly anion and an $NH_3^+$-MIL-101 cation. As the result of ICP analysis, it was found that the prepared PWA-$NH_2$-MIL-101 was supported with 50 wt% of PWA.

[91] <Example 8> Preparation of $HO_3S$-MIL-101 functionalized with sulfonic acid group

[92] An AMS-MIL-101, in which amino groups are bonded to the coordinatively unsaturated metal sites thereof and sulfonic acid is functionalized, was prepared by refluxing the mixed solution, using the same method as in Example 1, except that

4-aminobenzenethiol (ABT) is used as an amphoteric functional group. It was found that the amino group (-$NH_2$) was present in the frequency range of 3200-3400 $cm^{-1}$ and that the S=O symmetric bond was present in the frequency range of 1150 $cm^{-1}$.

[93] <Example 9> Base catalytic reaction

[94] A Knoevenagel condensation reaction, which is a base catalytic reaction in which ethyl trans-a-cyanocinnamate is formed using benzaldehyde (BZA, 10 mmol) and ethyl cyanoacetate (ECA) as reactants, was conducted using the porous organic-inorganic hybrid material ($NH_2$-MIL-101), which includes an aminosilane functional group and is coordinated with an alkoxy group, obtained in Example 2, Example 3 and Preparation Example 2. The results of the reaction are given in Table 1. As given in Table 1, it was found that the reaction product has excellent activity as a base catalyst, compared to the APS-SBA-15, which is pretreated at a temperature of 150°C and thus surface-functionalized in Preparation Example 2.

[95] Table 1

[Table 1]

[Table ]

Comparison of catalytic activity in Knoevenagel condensation reaction

| Sample | Surface area ($m^2/g$) | Yield(%)[a] | TOF[b]($h^{-1}$) |
|---|---|---|---|
| Example 2 | 2216 | 97.7 | 370.5 |
| Example 3 | 1792 | 97.7 | 211.7 |
| Preparation Example 2 | 340 | 73.3 | 32.1 |

[96] a. conversion ratio of ECA: reaction time 16 hr, amount of catalyst 20 mg

[97] b. TOF (Turnover Frequency): product (mole)/ catalyst (mole), reaction time 20 min

[98] <Example 10> Catalytic reaction using precious metal

[99] A C-C bond formation reaction (Heck reaction), in which trans-stilbene is formed using iodobenzene and styrene, was conducted using the Pd-$NH_2$-MIL-101 supported with palladium, obtained in Example 5. As the results of the reaction, it was found that the reaction product has at least two times the catalytic activity of the Pd-APS-SBA-15 in the C-C bond formation reaction because the coordinatively unsaturated metal sites thereof are functionalized with palladium.

[100] <Example 11> Acid catalytic reaction

[101] An esterification reaction, in which ethyl acetate is formed using acetic acid (0.03

mol) and ethanol (0.3 mol) as reactants through an acid catalytic reaction, was conducted using 0.05 g of AMS-MIL-101 obtained in Example 4. As the result of the reaction, it was found that the reaction product has at least three times the catalytic activity of the MIL-101 of Preparation Example 1 in the esterification reaction because the coordinatively unsaturated metal sites thereof are functionalized with acidic functional groups.

[102] <Example 12> Preparation of porous organic-inorganic hybrid material (MIL-101) thin film functionalized with amino group

[103] $Cr(NO_3)_3.9H_2O$, an aqueous HF solution and 1,4-benzenedicarboxylic acid (BDCA) were put into a Teflon reactor, and then distilled water was added thereinto such that the final molar ratio of the reactant mixture is $Cr:HF:BDCA:H_2O=1:1:1:275$. Thereafter, an alumina substrate was aligned perpendicular to the mixed solution, and then the Teflon reactor including the reactant mixture and the alumina substrate was mounted in a microwave reactor (manufactured by CEM Ltd., Mars-5) and then irradiated with microwaves for 3 minutes to increase the temperature of the reactant mixture to 180 ℃. Subsequently, the reactant mixture was left at a temperature of 180℃ for 30 minutes to react, was cooled to room temperature, was cleaned using distilled water, and was then dried, thereby obtaining the organic-inorganic hybrid material (MIL-101) thin film. The X-ray diffraction patterns (XRD patterns) of the obtained MIL-101 thin film corresponded to those of the conventional powder synthesis research (Science 2005, 309, 2040), in which the MIL-101 is synthesized in an electric oven at a temperature of 220℃ for 10 hours. The MIL-101 thin film was perpendicularly fixed to the bottom of a reflux reactor in which a mixed solution of 1 ml of 3-aminopropyltriethoxysilane (APS) and 50 ml of toluene was placed. Subsequently, the mixed solution was refluxed at a temperature of 110℃ for 12 hours, thereby preparing a porous organic-inorganic hybrid material thin film coordinated with ethoxy functional groups to the unsaturated sites thereof.

# Claims

[1] A method of preparing a surface-functionalized porous organic-inorganic hybrid material by reacting a porous organic-inorganic hybrid material or an organic-inorganic mesoporous material having unsaturated metal sites with one or more selected from among an organic substance, an inorganic substance, an ionic liquid, and an organic metal compound.

[2] The method according to claim 1, wherein the porous organic-inorganic hybrid material is a crystalline polymer compound formed by bonding an organic ligand with a central metal ion and has a molecule-sized pore structure or a nanosized pore structure, and

the organic-inorganic mesoporous material is a mesoporous molecular sieve having unsaturated metal sites substituted with different metals.

[3] The method according to claim 2, wherein the precursor of the central metal ion of the porous organic-inorganic hybrid material is one or more metals selected from among Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Mg, Ca, Sr, Ba, Sc, Y, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb and Bi, or metal compounds thereof.

[4] The method according to claim 2, wherein an organic material, serving as the ligand, is a compound having one or more functional groups selected from among a carboxylic acid group, a carboxylic acid anion group, an amino group, an imino group, a sulfonic acid group, a sulfonic acid anion group, a methane dithionic acid group, a methane dithionic acid anion group, a pyridine group and a pyrazine group, or mixtures thereof.

[5] The method according to claim 4, wherein the compound having the carboxylic acid is one or more selected from among benzene dicarboxylic acid, naphthalene dicarboxylic acid, benzene tricarboxylic acid, naphthalene tricarboxylic acid, pyridine dicarboxylic acid, bipyridyl dicarboxylic acid, formic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, hexanedioic acid, heptanedioic acid, and cyclohexyl dicarboxylic acid.

[6] The method according to claim 2, wherein the porous organic-inorganic hybrid material has a thin film structure or a membrane structure.

[7] The method according to claim 1, wherein the organic substance is one or more compounds selected from among compounds represented by Formulas 1 to 3 below:

[Formula 1]

$H_2N$-M-R1

[Formula 2]

HS-M-R2

[Formula 3]

$(OH)_2OP$-M-R3

wherein M is an alkylene or aralkylene group of $C_1$~$C_{20}$ including unsaturated hydrocarbons or including no unsaturated hydrocarbons, and each of $R^1$, $R^2$ 또는 $R^3$is independently an organic alkylene or aralkylene group, unsubstituted or substituted with one or more selected from among halogen elements, a vinyl group (-C=$CH_2$), an amino group (-$NH_2$), an imino group (-$NHR^{14}$), a mercapto group (-SH), a hydroxyl group (-OH), a carboxylic acid group (-COOH), a sulfonic acid group (-$SO_3H$), an alkoxy group (-OR) and a phosphoric group (-$PO(OH)_2$).

[8] The method according to claim 1, wherein the inorganic substance is polyoxometallate of $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]_{7+}$ or $[PW_{12}O_{40}]^{4-}$, and
the polyoxometallate is one or more selected from among a Keggin structure anion $[(XM_{12}O_{40})^{n-}$, where n is an integer of 1 ~ 10; X is P, Si, H, Ga, Ge, V, Cr, Me or Fe; and M is one or more selected from among W, Mo, and Co], a Lindqvist structure anion $[(M_6O_{19})_{n-}$, where n is an integer of 1 ~ 10; and M is W, Mo, Ta, V or W], an Anderson-Evans structure anion $[(M_x(OH)_6M_6O_{18})^{n-}$, where n is an integer of 1 ~ 10; Mx is Cr, Ni, Fe, or Mn; and M is Mo, or W] or $[(M_4(H_2O)_4(P_2W_{15}O_{56})_2)^{n-}$, where n is an integer of 1 ~ 10; and M is one or more transition metals or transition metal clusters selected from among Cu, Zn, Ni, Mn, and the like], and Dawson-Wells structure $(P_2W_{15}O_{56})_2$.

[9] The method according to claim 1, wherein the ionic liquid is one or more salts selected from among ammonium, Phosphonium, Sulphonium, Pyrrolidinium, Imidazolium, Thiazolium, Pyridium and Triazolium.

[10] The method according to claim 1, wherein the organic-inorganic hybrid material is one or more selected from among compounds represented by Formulas 4 to 11 below:

[Formula 4]

$Si(OR^1)_{4-x}R_x$ ($1 \le x \le 3$)

[Formula 5]

$Si(OR^3)_{4-(y+z)}R^2_yZ_z$ ($1 \le y+z \le 3$)

[Formula 6]

$Si(OR^4)_{4-a}R^5_aSi$ $(1\leq a\leq 3)$

[Formula 7]

$Z^1_b(OR^6)_{3-b}Si\text{-}A\text{-}Si(OR^7)_{3-C}Z^2_C$ $(0\leq b\leq 2,\ 0\leq c\leq 2)$

[Formula 8]

$R^8_eM^1(OR^9)_{4-e}$ $(1\leq e\leq 3)$

[Formula 9]

$R^{10}_gM^2Z^3_f(OR^{11})_{4-(f+g)}$ $(1\leq f+g\leq 3)$

[Formula 10]

$M^3(OR^{12})_h$ $(1\leq h\leq 2)$

[Formula 11]

$M^4(OR^{13})_iZ^4_j$ $(1\leq i+j\leq 2)$

wherein A is an alkylene or aralkylene group of $C_1$~$C_{20}$ including unsaturated hydrocarbons or not including unsaturated hydrocarbons, each of $Z^1$, $Z^2$, $Z^3$ and $Z^4$ is independently selected from among halogen elements, each of $M^1$ and $M^2$ is independently one or more elements selected from among transition metals, Lanthanides and Actinides, each of $M^3$ and $M^4$ is independently one or more elements selected from among alkali metals and alkaline earth metals, each R and $R^1$ to $R^{13}$ is independently an alkyl group, alkenyl group or alkynyl group of $C_1$~$C_{20}$, unsubstituted or substituted with one or more selected from among halogen elements, a vinyl group (-C=$CH_2$), an amino group (-$NH_2$), an imino group (-NHR$^{14}$), a mercapto group (-SH), a hydroxyl group (-OH), and a carboxylic acid group (-COOH), or is selected from among a vinyl group (-C=CH), an amino group (-$NH_2$), an imino group (-NHR$^{14}$), a mercapto group (-SH), a hydroxyl group (-OH) and a carboxylic acid group (COOH), and $R^{14}$ is an alkyl group, an alkenyl group or an alkynyl group of $C_1$~$C_{10}$, unsubstituted or substituted with halogen, an amino group, a mercapto group or a hydroxyl group.

[11] The method according to claim 1, further comprising:
Secondarily functionalizing the surface functionalized porous organic-inorganic hybrid material by reacting it with precious metals, transition metals, typical metals, or lanthanides.

[12] The method according to claim 11, wherein the surface functionalized porous organic-inorganic hybrid material is prepared using a typical electric oven heating method or a microwave heating method.

[13] The method according to any one of claims 1 to 12, further comprising:

supporting one or more metals selected from among precious metals, transition metals, typical metals and Lanthanides, or oxides thereof on the surface functionalized porous organic-inorganic hybrid material.

[14] The method according to claim 13, wherein the porous organic-inorganic hybrid material is chromium terephthalate, iron terephthalate, vanadium terephthalate, aluminum terephthalate, chromium benzenetricarboxylate, iron benzenetricarboxylate, vanadium benzenetricarboxylate, or aluminum benzenetricarboxylate.

[15] The method according to claim 14, wherein the porous organic-inorganic hybrid material has MIL-101, MIL-100, and MOF-500 structures.

[16] A surface functionalized porous organic-inorganic hybrid material composition prepared using the method according to any one of claims 1 to 15.

[17] A catalyst composition comprising the surface functionalized porous organic-inorganic hybrid material prepared using the method according to any one of claims 1 to 16.

[18] The catalyst composition according to claim 17, wherein the catalyst composition is used for an acid-base reaction, hydrogenation, dehydrogenation, carbon-carbon bonding reaction, or oxidation reaction by oxygen, air or hydrogen peroxide.

# DRAWINGS

FIGURE 1

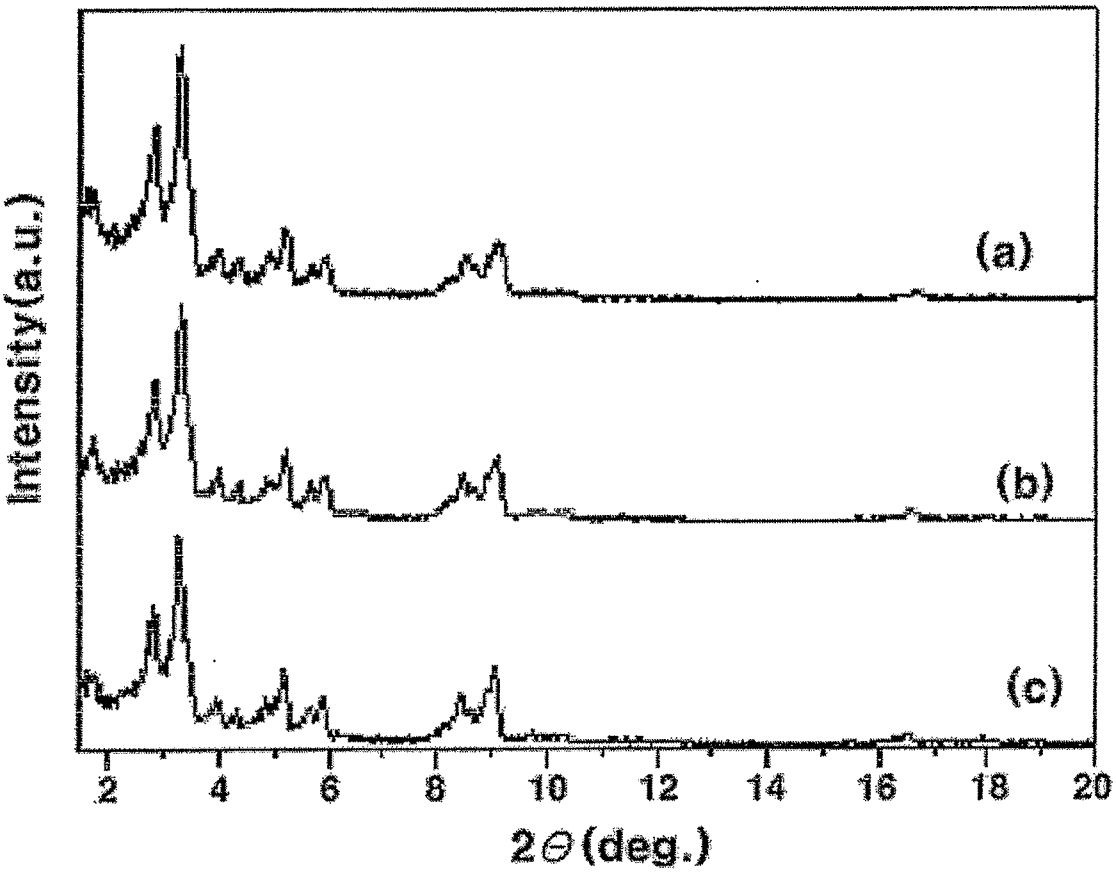


FIGURE 2

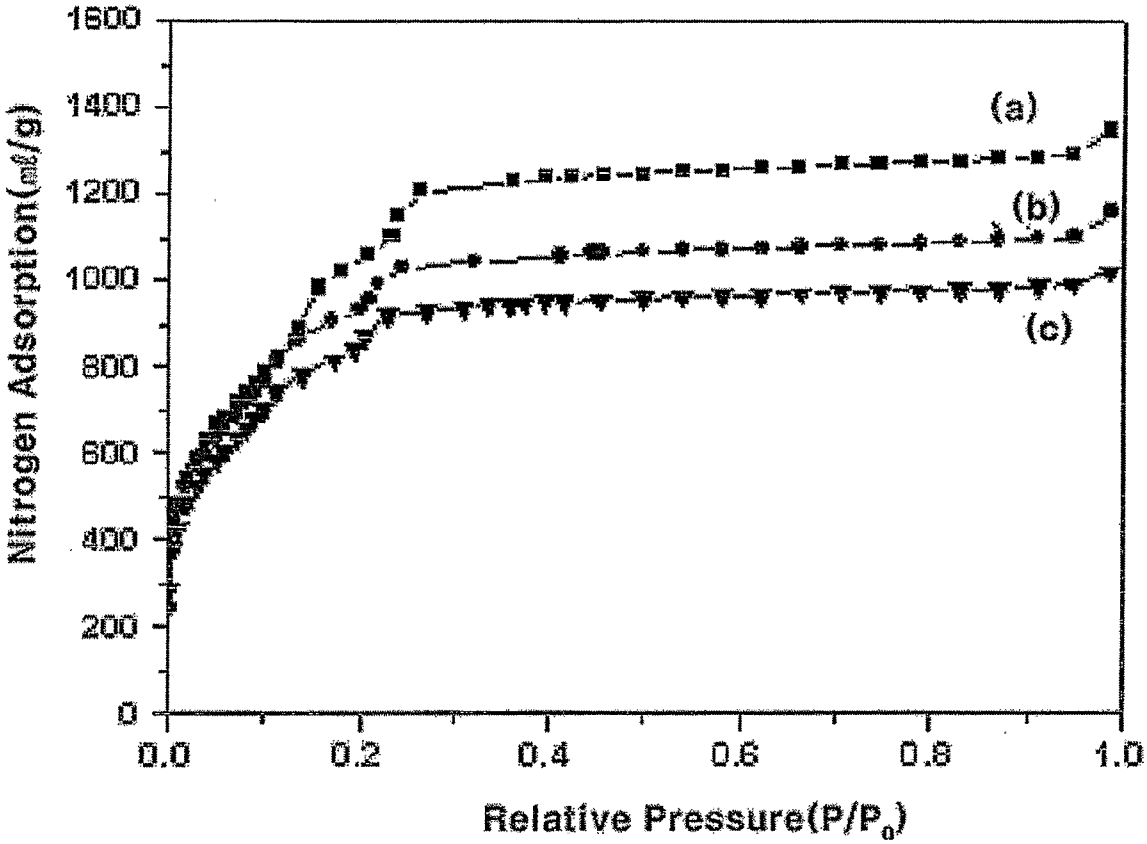

Nitrogen Adsorption(㎖/g)
1600
1400
1200
1000
800
600
400
200
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure(P/P0)
(a)
(b)
(c)

FIGURE 3

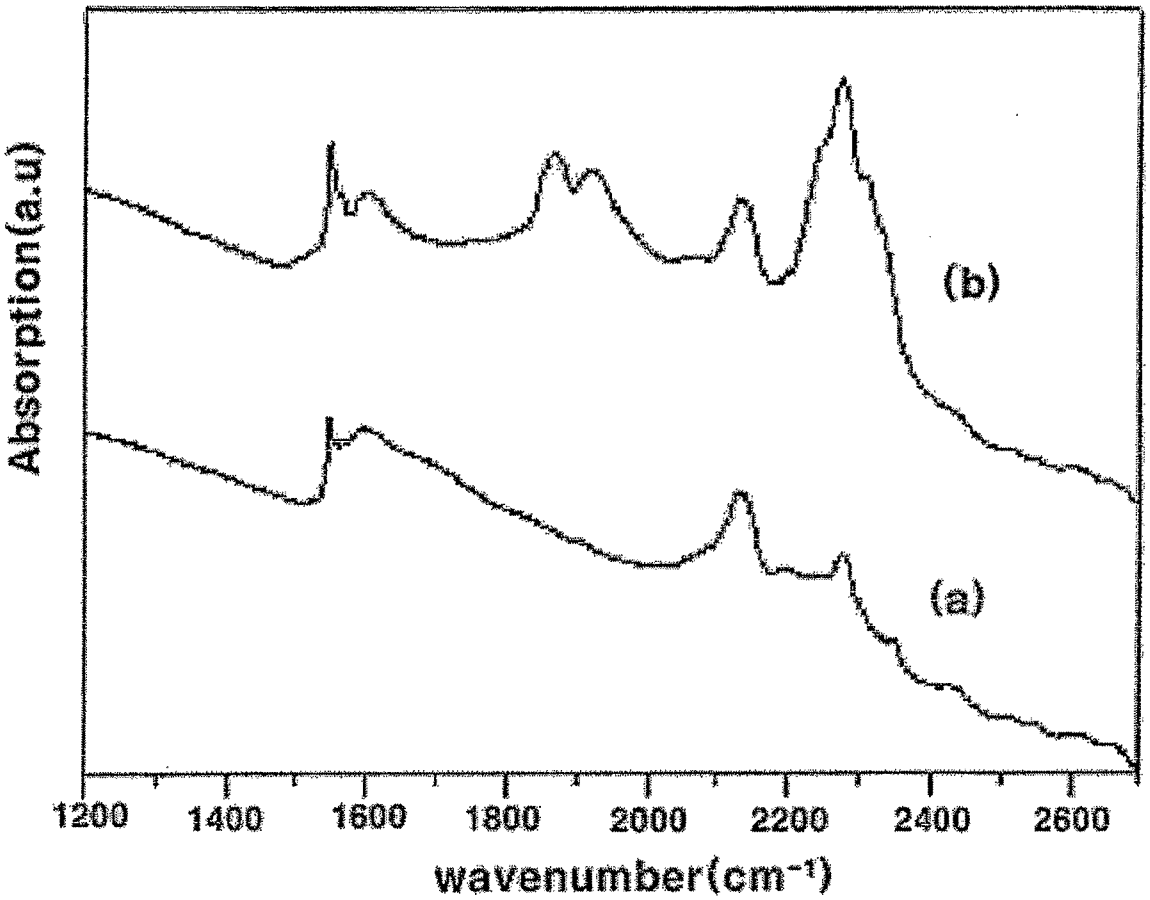

Absorption(a.u)
(b)
(a)
1200
1400
1600
1800
2000
2200
2400
2600
wavenumber(cm⁻¹)

FIGURE 4

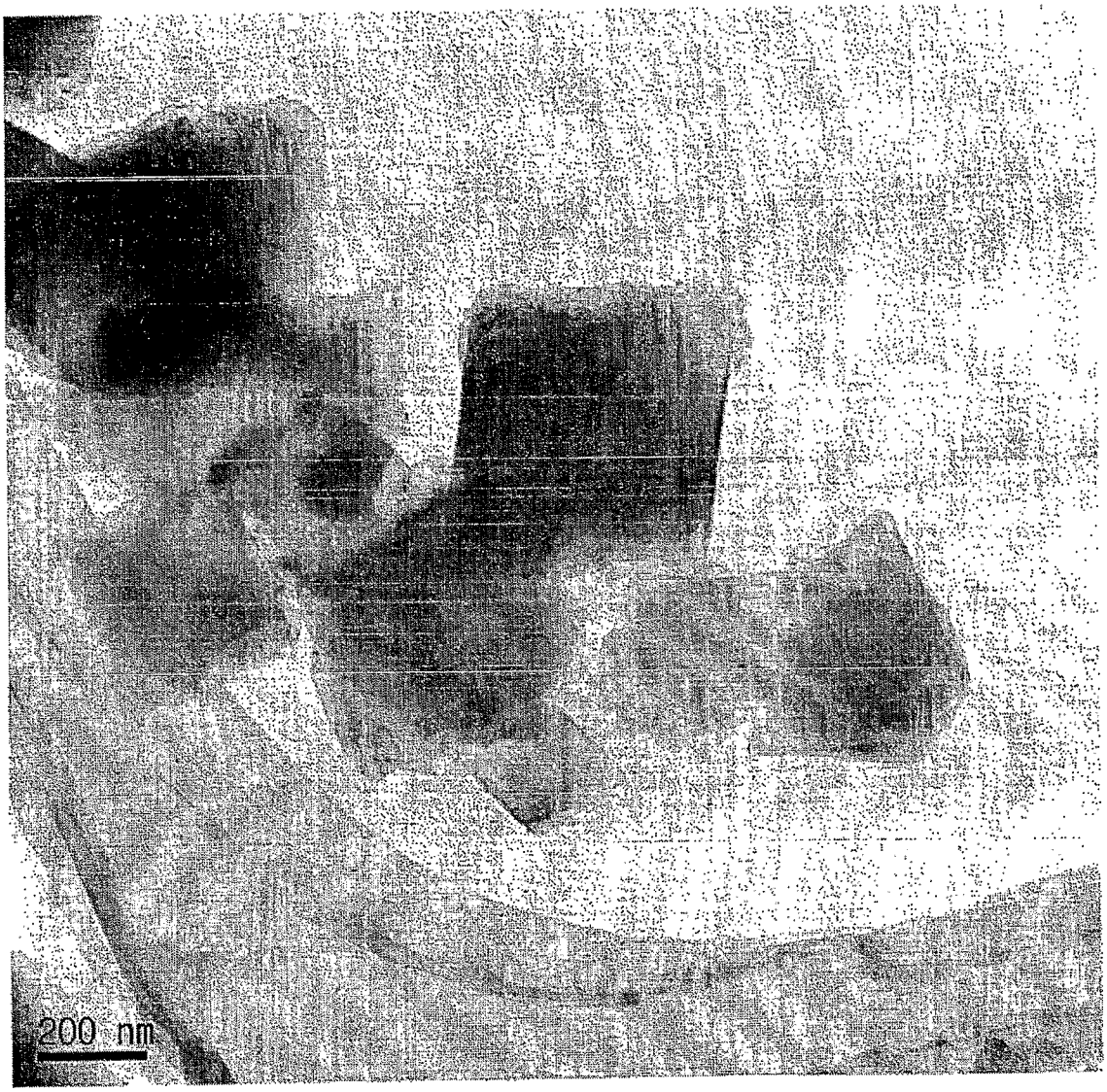
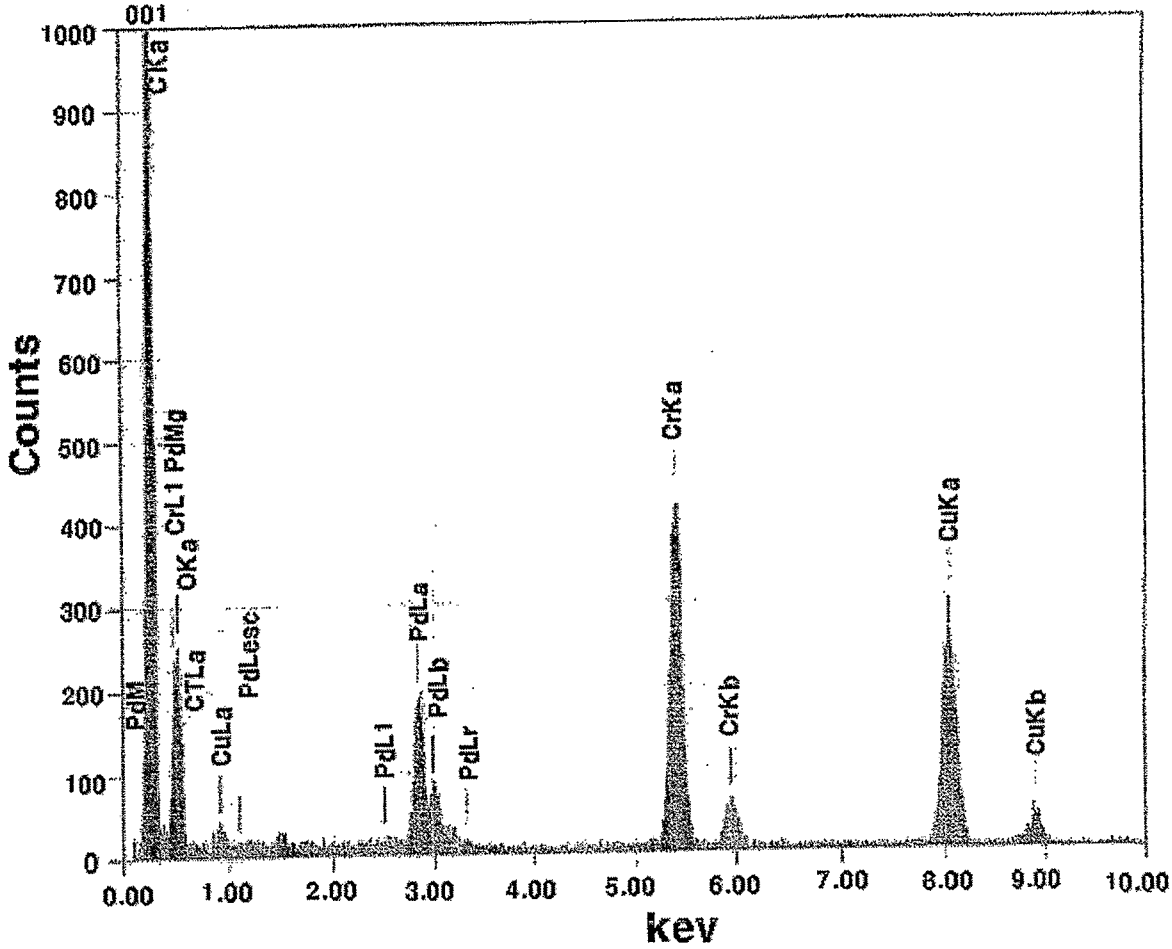


FIGURE 5


001
CtKa
PdMg
CrL1
OKa
CTLa
CuLa
PdLesc
PdM
PdL1
PdLa
PdLb
PdLr
CrKa
CrKb
CuKa
CuKb
Counts
kev
1000
900
800
700
600
500
400
300
200
100
0
0.00
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10.00

**INTERNATIONAL SEARCH REPORT**

International application No.
**PCT/KR2007/006431**

**A. CLASSIFICATION OF SUBJECT MATTER**

***B01J 31/12(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 : C08F 2/38

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

Korean Utility models and applications for Utility models since 1975

Japanese 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(KIPO internal) "porous", "hybrid", "metal", "unsaturate", "ligand", "chelate", "organic-inorganic"

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP 2006225579 A (SUMITOMO Chemical Co., Ltd.) 31 Aug. 2005<br>see claim 1-7 | 1-18 |
| A | JP 2004285315 A (NIPPON SHOKUBAI Co., Ltd.) 14 Oct. 2004<br>see claim 1-7 | 1-18 |
| A | US 20060252641 A1 (OMAR M. Yaghi et al) 09 Nov. 2006<br>see calim 1-48 | 1-18 |
| A | KR 100680767 B1 (KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY) 09 Feb. 2007<br>see claim 1-4, 12-16 | 1-18 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

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"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 | Date of mailing of the international search report |
|---|---|
| 13 MARCH 2008 (13.03.2008) | **13 MARCH 2008 (13.03.2008)** |


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Authorized officer

Na, Young Min

Telephone No. 82-42-481-8394

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/KR2007/006431**

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| JP 2006225579 A | 2006.08.31. | JP 18225579 | 2006.08.31. |
| | | JP 18225579 | 2006.08.31. |
| | | JP 2006225579 A2 | 2006.08.31. |
| | | US 2006189770 AA | 2006.08.24. |
| | | US 7109279 BB | 2006.09.19. |
| JP 2004285315 A | 2004.10.14. | CN 1458144 A | 2003.11.26. |
| | | EP 01362637 A1 | 2003.11.19. |
| | | JP 16285315 | 2004.10.14. |
| | | JP 2004285315 A2 | 2004.10.14. |
| | | KR 1020030088867 | 2003.11.20. |
| | | US 2004014598 AA | 2004.01.22. |
| | | US 7009066 BB | 2006.03.07. |
| US 20060252641 A1 | 2006.11.09. | None | |
| KR 100680767 B1 | 2007.02.09. | WO 2007091828 A1 | 2007.08.16. |