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(54) Title: COMPOSITIONS AND METHODS OF MAKING AND USING METAL-ORGANIC FRAMEWORK COMPOSITIONS

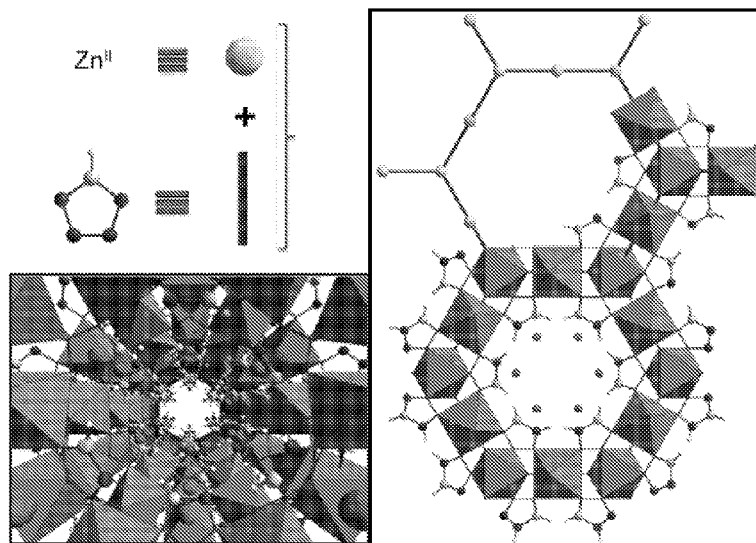


FIGURE 1

(57) Abstract: Embodiments of the present disclosure include a metal-organic framework (MOF) composition comprising one or more metal ions, a plurality of organic ligands, and a solvent, wherein the one or more metal ions associate with the plurality of organic ligands sufficient to form a MOF with kag topology. Embodiments of the present disclosure further include a method of making a MOF composition comprising contacting one or more metal ions with a plurality of organic ligands in the presence of a solvent, sufficient to form a MOF with kag topology, wherein the solvent comprises water only. Embodiments of the present disclosure also describe a method of capturing chemical species from a fluid composition comprising contacting a MOF composition with kag topology and pore size of about 3.4Å to 4.8Å with a fluid composition comprising two or more chemical species and capturing one or more captured chemical species from the fluid composition.

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COMPOSITIONS AND METHODS OF MAKING AND USING METAL-ORGANIC FRAMEWORK COMPOSITIONS

BACKGROUND

[0001] Gas/vapor separation represents a large share of processing in oil, petrochemical, nuclear and many other industries. Gas/vapor separation related to upstream and downstream of natural gas (NG) processing is often very complex and challenging, particularly at the stage of sweetening (removal of acid gases (CO₂, H₂S)), dehydration and BTX (Benzene, Toluene and Xylenes) removal.

[0002] The control of greenhouse gases is of societal importance because it is well recognized that it has a significant impact on climate change. Among all the greenhouse gas emissions, CO₂ has received the most attention due to the large quantities of man-made emissions in the atmosphere. The CO₂ atmospheric concentration has exploded to reach record levels in May 2013 of 400 parts per million (ppm), which is an unprecedented level in human history. For years, the scientific community has focused its efforts to develop different strategies to mitigate the undesirable CO₂ emissions in the atmosphere from industrial activities (particularly emissions of CO₂ originating from the burning of fossil fuels) and transportation. Therefore, CO₂ Capture and Storage (CCS) and CO₂ Capture and Use (CCU) are recognized as strategies to reduce the emissions of CO₂ from the atmosphere.

[0003] Among the handful of technologies that tackle this challenge, cryogenic distillation and liquid amine scrubbing are the dominant methods. Nevertheless, these technologies are highly energy intensive, hence not cost effective. Adsorption is currently recognized as one of the alternative separation technologies that can address capturing the CO₂ challenge, taking into account both technical and cost effectiveness. Therefore, the choice of the suitable adsorbents that drives the separation process is of prime importance. Many materials have been investigated for their properties to adsorb CO₂ selectively, which includes zeolites, carbon based materials and metal-organic frameworks.

SUMMARY

[0004] Embodiments of the present disclosure include a metal-organic framework (MOF) composition comprising one or more metal ions, a plurality of organic ligands, and a solvent,

wherein the one or more metal ions associate with the plurality of organic ligands sufficient to form a MOF with kag topology.

[0005] Embodiments of the present disclosure further include a method of making a MOF composition comprising contacting one or more metal ions with a plurality of organic ligands in the presence of a solvent, sufficient to form a MOF with kag topology, wherein the solvent comprises water only.

[0006] Embodiments of the present disclosure also describe a method of capturing chemical species from a fluid composition comprising contacting a MOF composition with kag topology and pore size of about 3.4Å to 4.8Å with a fluid composition comprising two or more chemical species and capturing one or more captured chemical species from the fluid composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 illustrates a schematic representation of a 3D kagomé tiling network (color scheme: Zinc = cyan, Nitrogen = blue, Carbon = grey, Oxygen = red, Hydrogen = white), according to some embodiments.

[0008] Figures 2A-B illustrate graphical views of (A) Adsorption of CO₂, H₂S, CH₄ and N₂ on kag-MOF, (B) isosteric heat of adsorption of H₂O vapour, CO₂ and CH₄, according to some embodiments.

[0009] Figure 3 illustrates a graphical view of adsorption of H₂O on kag-MOF at 298K after evacuation at 393 K, according to some embodiments.

[0010] Figure 4 illustrates a graphical view of adsorption of H₂S as compared to benzene on kag-MOF at low pressures (No benzene is adsorbed), according to some embodiments.

[0011] Figure 5 illustrates a graphical view of experimental and calculated powder X-ray diffraction patterns indicating the phase purity and stability of kag-MOF at different thermal and chemical conditions, according to some embodiments.

[0012] Figure 6 illustrates a graphical view of TGA of kag-MOF, according to some embodiments.

[0013] Figure 7 illustrates a graphical view of comparison of IR spectrum of the as-synthesized kag-MOF vs ligand, according to some embodiments.

[0014] Figures 8A-D illustrate schematic representations of 2D kagomé tiling networks, according to some embodiments.

[0015] Figure 9 illustrates a graphical view of CO₂ adsorption (filled circles)-desorption (open circles) isotherm on kag-MOF at 273 K (evacuation at 393 K). The inset shows the pore size distribution determined using NLDFT, according to some embodiments.

[0016] Figure 10 illustrates a graphical view of variable temperature isotherms on kag-MOF after evacuation at 393K, according to some embodiments.

[0017] Figure 11 illustrates a graphical view of CO₂ adsorption isotherms on kag-MOF at 298 K after evacuation at 328, 393 and 433 K, according to some embodiments.

[0018] Figure 12 illustrates a graphical view of Q_{st} of CO₂ adsorption on kag-MOF after evacuation at 323 and 393 K, according to some embodiments.

[0019] Figure 13 illustrates a graphical view of variable temperature CO₂ adsorption isotherms on kag-MOF after evacuation at 323 K, according to some embodiments.

[0020] Figure 14 illustrates a graphical view of variable temperature CH₄ adsorption isotherms on kag-MOF after evacuation at 393 K, according to some embodiments.

[0021] Figures 15A-B illustrate a graphical views of (A) IAST prediction for CO₂/N₂, CO₂/CH₄ mixtures, (B) Column breakthrough test for CO₂/N₂:10/90 mixture adsorption at 298 K and 1 bar total pressure, according to some embodiments.

[0022] Figures 16A-B illustrate graphical views of (A) pure component CO₂ N₂, CH₄ at 298K (B) Q_{st} of CO₂ and CH₄ adsorption after activation at 55°C and 120°C, according to some embodiments.

[0023] Figure 17 illustrates a graphical view of Density of CO₂ adsorbed at 298 K, according to some embodiments.

[0024] Figure 18 illustrates a graphical view of Variable Temperature PXRD patterns of kag-MOF, according to some embodiments.

[0025] Figure 19 illustrates a graphical view of PXRD patterns of kag-MOF after soaking in different solvents for 24 h as evidence of the stability of kag-MOF, according to some embodiments.

DETAILED DESCRIPTION

[0026] In general, embodiments of the present disclosure describe metal organic framework compositions, and methods of making and using MOF compositions. In particular, the present disclosure describes embodiments including a highly stable metal organic framework composition fabricated in water without any other solvent and with a low-cost reagent, such as tetrazolate and zinc salts. This MOF platform is a highly stable, nitrogen-rich MOF made in water for multipurpose use in gas/vapor separations, such as dehydration, CO₂ capture,

H₂S removal and BTX sieving from natural gas. The MOFs of the present embodiments can be synthesized in water without any other solvent, with simple process steps and low-cost chemicals, such as zinc salt and tetrazolate based ligand. The MOF compositions of the present disclosure include a kagomé (kag) topology. The kag-MOF composition is highly stable and exhibits suitable properties for CO₂ from flue gas and natural gas in dry conditions. The compositions described herein show an excellent balance between selectivity, CO₂ uptake and energy for regeneration. Additionally, the compositions include desiccant properties, particularly with a low energy for dehydration. The kag-MOF compositions can also successfully and substantially perform H₂S/CH₄, H₂S/BTX and acetone/phenol separation and gas dehydration.

[0027] Although many N-containing MOFs have been reported, systematic studies on CO₂ capture in concurrent correlation to pore size are scarce. Embodiments here describe efforts to tune/design novel materials for CO₂ capture, such as developing several strategies to enhance the CO₂ energetics in MOFs. As a first example, rht-MOF-7, fabricated by deliberate modification of the trigonal core of the parent rht-MOF-1 by a triazine core linked to an amine functional group in between the core and isophthalate termini, was found to be excellent candidate platforms for systematic enhancement of CO₂ capture efficiency. The resulting synergetic effect of N-containing ligand and secondary amine was reflected by a drastic enhancement of the isosteric heat of CO₂ adsorption at low loading (44.7 kJ mol⁻¹ versus 35 kJ mol⁻¹ for the parent rht-MOF-1), albeit with a subsequent sharp decrease, mainly because of the quick saturation of the highly energetic sites, but non-homogeneous, and the occurrence of pore filling which follows.

[0028] In a second example, the assembly of rare-earth based (terbium) fcu platform by utilizing polarized ligands containing tetrazolate and fluoro moieties positioning in a close vicinity of open metal sites, has resulted in very high CO₂ energetics as the initial Q_{st} at low loading was 58.1 kJ mol⁻¹. Similar to the rht platform, the amount of highly energetic sites was limited and non-homogeneously distributed. In both cases, rht and fcu platforms possess quite big cavities (10.4 and 17.8 Å in the former and 14.5 and 9.1 Å, respectively), therefore the CO₂ adsorption occurs first on the most active (limited) sites which saturate quickly leading in turn to a drastic decrease in selectivity toward CO₂.

[0029] In another example, a reticular chemistry approach aiming to build an extended/contracted series of channel based MOFs constructed with bipyridyne/Cu and pyrazine/Zn 2-D periodic 4×4 square grids pillared by SiF₆ anions, led to the unveiling of an effective adsorption mechanism combining both thermodynamics and energetics. In fact, the

contracted analogue assembled from zinc (or copper) cation and pyrazine ligand, characterized by channels with small pore diameter of 3.84Å (SIFSIX-3-Zn), showed high and uniform Q_{st} for CO₂ at 45-52 kJ mol⁻¹ throughout the loading, affording unprecedented physical adsorbent with high selectivity towards CO₂ at various concentrations. With this foundation, embodiments of the present disclosure are then directed to a new MOF material with small-channeled pores, assembled using nitrogen-rich polarizable ligand.

[0030] The kag-MOFs described herein can utilize green-synthesis methods for synthesizing porous materials, which reduce or eliminate the need for solvents and corrosive metal salt reagents, reduce or eliminate toxic and/or acidic byproducts, and are scalable to industrial levels. The future deployment of MOF materials at the larger scale for many applications such as adsorbents, catalysts, and sensors, among many others, require clean, environmentally friendly, easy, cost efficient and scalable synthesis procedures. Solution-based MOF synthesis methodologies, such as the solvothermal method previously discussed, suffer from the need to use toxic and/or corrosive metal salts reagents. In addition to being costly and hazardous, these reagents further generate acid byproducts, which are often susceptible to solvolysis and require costly disposal. The need for fresh solvents, enhanced safety precautions, and waste disposal greatly increases both the capital costs and production costs of these methods. Low reproducibility further precludes industrial applications of solvothermal synthesis methods.

[0031] Metal organic frameworks (MOFs) are a versatile and promising class of crystalline solid-state materials that allow porosity and functionality to be tailored towards various applications.

[0032] Generally, MOFs comprise a network of nodes and ligands, wherein a node has a connectivity capability at three or more functional sites, and a ligand has a connectivity capability at two functional sites each of which connect to a node. Nodes are typically metal ions or metal containing clusters, and, in some instances, ligands with node connectivity capability at three or more functional sites can also be characterized as nodes. In some instances, ligands can include two functional sites capable of each connecting to a node, and optionally one or more additional functional sites, which do not connect to nodes within a particular framework. In some embodiments, ligands can be poly-functional, or polytopic, and comprise two or more functional sites capable of each connecting to a node. In some embodiments, polytopic ligands can be heteropolytopic, wherein at least two of the two or more functional sites are different.

[0033] Embodiments of the present disclosure describe a metal-organic framework composition comprising one or more metal ions, an organic ligand, and a solvent, wherein the

one or more metal ions associate with the organic ligand sufficient to form a MOF with kag topology. The one or more metal ions may include M^{2+} cations. The M^{2+} cations may include one or more of Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} . The organic ligand may be an inexpensive organic building block. The organic ligand may include any N donor ligand. For example, the organic ligand may include one or more of tetrazole, triazole, derivatives of tetrazole, and derivatives of triazole. The one or more metal ions may associate with the organic ligand to form a metal-organic framework with kagomé topology (kag-MOF). (Figure 1) In some embodiments, the kag-MOF includes a plurality of organic ligands. In some embodiments, the kag-MOF is formed in the presence of a solvent, wherein the solvent includes water or is only water. In some embodiments, the kag-MOF may be hydrothermally synthesized. In other embodiments, the kag-MOF may be highly stable. In another embodiment, the kag-MOF may be hydrothermally synthesized and highly stable.

[0034] The kag-MOF of the present disclosure may include any combination of M^{2+} cations – including, but not limited to, one or more of Zn^{2+} , Cu^{2+} , Ni^{2+} , and Co^{2+} – with any combination of organic ligands – including, but not limited to, one or more of tetrazole, triazole, derivatives of tetrazole, and derivatives of triazole. In some embodiments, the kag-MOF may include one of the above-mentioned metal cations or a mixture of metal cations, with one of the above-mentioned organic ligands, a mixture of organic ligands, a plurality of the above-mentioned organic ligands, or a plurality of a mixture of organic ligands.

[0035] Embodiments of the present disclosure also include methods of making a MOF composition. The method of making a MOF composition may include contacting one or more metal ions with an organic ligand sufficient to form a MOF with kag topology. In other embodiments, the method of making a MOF composition may include contacting one or more metal ions with a plurality of organic ligands sufficient to form a MOF with kag topology. In another embodiment, the method of making a MOF composition may include contacting one or more metal ions with an organic ligand or a plurality of organic ligands in the presence of a solvent. In some embodiments, the solvent includes water or is water only.

[0036] Embodiments of the present disclosure further include a method of capturing chemical species from a fluid composition. The method may include contacting a MOF composition with kag topology and pore size of about 3.4Å to 4.8Å with a fluid composition comprising two or more chemical species and capturing one or more captured chemical species from the fluid composition. The MOF composition with kag topology may include any of the

embodiments described above. The chemical species captured by the kag-MOF may include one or more of CO₂, H₂S, H₂O, and acetone. In some embodiments, CO₂ is the captured chemical species from a fluid composition including one or more of natural gas, flue gas, syngas, biogas, and landfill gas. In other embodiments, H₂S is the captured chemical species from a fluid composition including one or more of H₂S, benzene, toluene, and xylene. In other embodiments, H₂O is the captured chemical species from a fluid composition including one or more of a gas, a vapor, and a solvent. In other embodiments, acetone is the captured chemical species from a fluid composition including one or more of acetone, phenol, and C₄ fractions. These embodiments are not limiting, and additional embodiments are provided below.

[0037] The kag-MOF described in these embodiments exhibits high chemical and thermal stability based on the kagomé platform. The particular synergetic effect of highly dense, homogeneously distributed tetrazoles, zinc cations and small pore size of channels, directed the homogeneous and fairly high interactions with CO₂, in one example. Embodiments herein confirm the high importance of the synergy between at least two driving forces, namely N-rich containing ligand and small pore size, to achieve the desired materials for capturing CO₂, H₂S, H₂O, and acetone. Owing to its facile hydrothermal synthesis, stability and structural properties, applications may utilize this kagomé platform-based MOF as a membrane for various gas separations based on molecular sieving effect.

[0038] The kag-MOF of the present disclosure exhibited high chemical and hydrothermal stability. The synergetic effect of the charges densely and uniformly distributed over the pore channels (Figure 1) and contracted pore size ranging from about 3.4Å to 4.8Å led to quite strong and steady CO₂ isosteric heat of physical adsorption translated into highly uniform CO₂ interaction within the framework, a key feature that directs the efficiency of CO₂ capture using adsorbents in dry conditions (Figure 2). As seen from Figure 2a, the measurement of H₂S up to 0.1 bar (partial pressure) shows that the steepness of the adsorption isotherm in case of H₂S is almost similar to CO₂, the H₂S in this case is adsorbed strongly and reversibly. H₂S adsorbs preferentially over CO₂ using kag-MOF.

[0039] The heat of adsorption of CO₂, CH₄ and H₂O shows that H₂O interacts strongly (58 kJ/mol) with the framework of kag-MOF as compared to CO₂ (36 kJ/mol) and CH₄ (12.5 kJ/mol) (Figure 2b). Therefore, it is expected that kag-MOF could be used also as an efficient gas dehydration agent (Figure 3) for industrial gases such as natural gas (NG). The best performing conventional materials for gas dehydration are 4A and 13X zeolites. For these zeolites, the energy necessary for reactivation (and subsequent

recycling) is twice as much (ca. 120 kJ/mol) as kag-MOF. This finding is important as dehydration of gases is a very energy intensive process and there is a large need for new dehydration agents to reduce the cost of water removal from industrial gases.

[0040] Once the CO₂ containing stream was water vapor and H₂S free, the kag-MOF was an excellent separation agent for CO₂ removal from flue gas and natural gas. This was confirmed experimentally using column breakthrough test performed using CO₂/N₂:10/90 mixture (Figures 15A-B). In fact, while CO₂ was retained in the column for 601s, the first N₂ signal was observed just after 2 s, indicative of the high CO₂ selectivity (520±200).

[0041] In light of the high H₂S adsorption capacity and the small channel size (aperture) of kag-MOF, the adsorption of benzene (one of the components of the undesirable BTX in natural gas) was studied to evaluate its equilibrium adsorption properties as compared to H₂S. Interestingly, benzene was shown not to adsorb on kag-MOF. See Figure 4, for example, illustrating a graphical view of adsorption of H₂S as compared to benzene on kag-MOF at low pressures, according to an embodiment of the present disclosure. This second finding shows that kag-MOF can potentially be used to sieve H₂S from BTX (Benzene, Toluene, Xylene).

[0042] Because of the sieving features of kag-MOF for benzene, it is believed that kag-MOF will be an excellent agent for the important separation of acetone from phenol and acetone from C₄.

[0043] Embodiments of the present disclosure include using kag-MOF compositions for H₂S removal from NG. The particular outstanding properties of kag-MOF materials in terms of stability, H₂S uptake and selectivity make this novel MOF suitable for many industrial applications where H₂S need to be removed, particularly NG which is of the extreme importance for the Kingdom of Saudi Arabia.

[0044] Embodiments of the present disclosure include using kag-MOF compositions for dehydration. The particular outstanding properties of kag-MOF in terms of stability to moisture, H₂O uptake and affinity make these series of novel MOFs suitable for many industrial applications where various degree of humidity need to be removed.

[0045] As discussed above, embodiments of the present disclosure include using kag-MOF compositions for CO₂ capture from NG. kag-MOF may be used as an efficient adsorbents for the removal of CO₂ at various concentration (from 1% to 20%) from dry and humid conditions relevant to industrial gases.

[0046] Embodiments of the present disclosure include using kag-MOF compositions for H₂S/BTX separation. The presence of aromatics such as benzene, toluene and xylene (BTX) as contaminants in H₂S gas stream entering Claus sulfur recovery units has detrimental effect on catalytic reactors, where BTX form soot particles, and clog and deactivate the catalysts. BTX removal before the BTX and H₂S containing stream enter the catalyst bed, could be a judicious solution to this problem. Because of the sieving affinity and its extremely high stability, kag-MOF may be used as a separation agent on PTSA (pressure-temperature swing system).

[0047] Embodiments of the present disclosure include using kag-MOF compositions for acetone/phenol and acetone/C₄ separation. The sieving property of kag-MOF for benzene inspired to launch a study for the separation of acetone from Phenol and C₄ fractions. kag-MOF is a potential material for this separation.

EXAMPLE: CO₂ Capture

[0048] The novel kagomé metal organic framework (MOF) with small pore size and N-rich linker was synthesized hydrothermally via coordination of tetrazole moieties with zinc cations which shows high chemical and thermal stability, as an example. The synergetic effect of the charges densely and uniformly distributed over the pore channels and contracted pore size led to quite strong and steady CO₂ isosteric heat of adsorption translated into highly uniform CO₂ interaction within the framework, a key feature that directs the efficiency of CO₂ capture using adsorbents.

[0049] MOFs represent a class of porous materials that offer high surface areas, permanent porosity and chemical tunability, making these materials suitable for adsorbing CO₂. However, designing stable MOFs with high selectivity towards CO₂ adsorption is still a challenging task. In fact, the affinity to CO₂ compared to other gases (N₂, CH₄, O₂, etc.) is one of the key factors influencing the economy of the CO₂ capture process. Hence, it is vital to tailor the functionality and the pore size of MOFs simultaneously in order to design novel materials specifically dedicated to CO₂. Intensive efforts are currently invested in the search of new strategies allowing the enhancement of binding energies between CO₂ molecules and the framework. (i) Incorporation of Lewis basic sites into MOFs (eg: amino groups), (ii) insertion of open metal sites and (iii) introduction of various other strongly polarizing functional groups are three approaches that are most frequently explored.

[0050] Indeed, hydrothermal reaction between Zn(NO₃)₂•3H₂O and tetrazole-5-carboxylate, ethyl ester yields a homogenous microcrystalline material. The as synthesized

compound was characterized and formulated by single crystal X-ray diffraction studies as $\text{Zn}_5(\text{HTet})_6(\text{Tet})_3(\text{OH})_7$. The purity of the material was confirmed by similarities between simulated and experimental powder X-ray diffraction (PXRD) (Figure 5) and elemental microanalysis. The crystallographic analysis states that a de-esterification occurs during the reaction. To confirm this contention, thermogravimetric analysis (TGA) was carried out under air (Figure 6) and the residue was analyzed by PXRD. The TGA shows two main drops corresponding to a total loss of 64.4% which is in good agreement with the theoretical data (62.1%). In addition, infrared spectroscopy measurements performed on the ligand clearly showed the presence of the ester group, with the characteristic $\nu_{\text{C=O}}$ band (1735 cm^{-1}) and the absence of the $\nu_{\text{C=O}}$ band of esters in the kag-MOF indicating the *in situ* de-esterification of the ligand during the synthesis. (Figure 7).

[0051] The compound crystallized in a hexagonal system (space group $\text{P6}_3/\text{mmc}$) and contained two crystallographic independent zinc cations, both coordinated to six nitrogen atoms of two independent tetrazole ligands to form octahedral surrounding. Neutral and deprotonated tetrazole ligands adopt tridentate and tetradentate coordination modes respectively. The assembly of the 6-connected $\text{Zn}(1)$ nodes and neutral tetrazole molecules result in the generation of 2D kagomé layers exhibiting hexagonal channels (Figure 8(a)). The packing of these layers along the *c* axis following the axial-to-axial pillaring, using $\text{Zn}(2)$ cations and deprotonated tetrazolates, yield a cationic 3D structure, balanced by hydroxide anions, with an overall kagomé tiling (kag) geometry (Figure 8). The framework exhibits 1D hydrophobic channels with a diameter of around 3.8 \AA (Figure 1).

[0052] Figure 8 describes (a) projection along (001) of the kagomé layer built up from $\text{Zn}(1)$ cations and neutral tetrazole molecules; (b) projection along (010) showing the packing of kagomé layers via deprotonated tetrazole molecules; (c) and (d) projection along (001) and (010) respectively of the structure showing the introduction of $\text{Zn}(2)$ cations within the structure.

[0053] Initial adsorption studies showed that N_2 and Ar probe the framework of the compound as non-porous at 77 and 87 K, respectively. This first result confirms, that indeed, the pore windows of this material are narrow, as was concluded from single crystal diffraction data. Accordingly, CO_2 measurement at 273 K was targeted as a primary methodology to confirm the permanent microporosity, as evidenced by the (fully reversible) type I CO_2 adsorption isotherm (Figure 9).

[0054] The specific BET surface area was estimated to be $211 \text{ m}^2 \cdot \text{g}^{-1}$ using CO_2 . The calculated theoretical total free pore volume was estimated to be $0.12 \text{ cm}^3 \cdot \text{g}^{-1}$. The pore

size distribution, calculated from CO₂ adsorption data at 273 K using non-Local density functional theory (NLDFT), was estimated to be very uniform, centered at diameter of 3.6 Å (Figure 9), in excellent agreement with single crystal diffraction data.

[0055] The uniformly distributed, exposed tetrazole combined with the reduced pore size of kag-MOF, are attractive features for evaluating the impact of pore size, shape and functionality on CO₂ adsorption energetics and uptake. Accordingly, CO₂ adsorption experiments were carried out at various adsorption and desorption temperatures (Figure 10) in order to look closely at the effect of total and partial evacuation of the framework on the CO₂ uptake and energetics. Prior to full adsorption study, optimization of activation protocol showed that kag-MOF can be fully evacuated at 393 K and further evacuation at 433 K resulted only a slight increase in the CO₂ uptake, particularly at 1 bar (Figure 11).

[0056] The isosteric heat of CO₂ adsorption, Q_{st} , was in turn calculated for the sample evacuated at 323K, 393 K (Figure 12). The Clausius–Clapeyron equation was used to process the adsorption data collected at temperatures between 258 and 298 K (Figure 13). Although a slight difference was observed in terms of uptake, the trends of the CO₂ Q_{st} as a function of loading were found to be similar after evacuation at 328 and 393 K (Figure 11). It is worth mentioning that the accuracy of the Q_{st} determination was confirmed by the established linearity of CO₂ isosters for the entire studied range of CO₂ loadings.

[0057] The Q_{st} of CO₂ adsorption is an intrinsic property that dictates the affinity of the pore surface toward CO₂, which in turn plays a major role in determining the adsorption selectivity and the necessary energy to release CO₂ during the regeneration step. As illustrated, kag-MOF exhibits quite high CO₂ affinity over a wide range of CO₂ loading (37.5 kJ.mol⁻¹) due to the homogeneously distributed strong adsorption sites. In light of the direct relationship of CO₂ and CH₄ adsorption energetics to CO₂/CH₄ adsorption selectivity, the Q_{st} of CH₄ adsorption was explored, determined from variable temperature CH₄ adsorption isotherms (Figure 14). In contrast to CO₂ energetics, CH₄ exhibits much lower Q_{st} at low loading (12.5 kJ.mol⁻¹) combined with decreasing trend as the uptake increased.

[0058] Elevated and uniform CO₂ interactions are the key to improve selectivity towards CO₂, which is a critical parameter for the effectiveness of gas separation and purification of important commodities from CO₂ (e.g., CH₄, N₂, H₂). Analysis of data using IAST (Figures 15A-B), shows that this material displays high CO₂/N₂ selectivity (ca. 700 at 1 bar for example) over a wide range of pressure while the calculated CO₂/CH₄ selectivity (88 at 1 bar) was comparatively low. In case of CO₂/N₂ mixture, the low N₂ adsorption uptake/energetics,

translated into low affinity for N₂ (Figure 15A) combined with the relatively strong energetics of CO₂ adsorption (Figures 16A-B), results in high equilibrium adsorption selectivity toward CO₂ (Figure 15B).

[0059] This result was confirmed experimentally using column breakthrough test performed using CO₂/N₂:10/90 mixture. In fact, while CO₂ was retained in the column for 601 s, the first N₂ signal was observed just after 2 s, indicative of the high CO₂ selectivity (520±200), which is in quite good agreement with the predicted results using IAST.

[0060] It is noteworthy to mention that the CO₂ uptake (volumetric and gravimetric) at the partial pressure of interest for post-combustion (1.26 mmol/g and 0.84 mmol/g at 0.1 bar for single gas and CO₂/N₂:10/90 mixture, respectively) is much lower for kag-MOF than the corresponding CO₂ uptake for the best MOF materials reported so far such as Mg-MOF-74, and SIFSIX-3-M. Nevertheless, the recorded density of CO₂ adsorbed phase is one of the highest for MOFs (Figure 17).

[0061] In addition to the efficiency of N₂ and CH₄ separation from CO₂, improving hydrothermal and chemical stability of MOFs in order to implement them in real-world conditions is another primordial ongoing key challenge for many MOFs. The thermal stability of the kag-MOF was evaluated using powder X-ray diffraction (PXRD) and maintains its crystallinity upon heating to temperatures up to 400°C (Figure 18). The same outstanding stability was observed after 24h soaking in water, boiling water, at different pH (Figure 5) and other organic solvents (Figure 19). All these results in addition to the rare hydrothermal nature of synthesis of kag-MOF confirm the exceptional thermal and chemical stability of the kag-MOF.

Experimental Methods: Synthesis of Zn₅(HTet)₆(Tet)₃(OH⁻)₇

[0062] A solution containing Zn(NO₃)₂•6H₂O (29.7 mg, 0.1 mmol), Tetrazole-5-ethylester (32.8 mg, 0.2 mmol), 4 ml H₂O was prepared in a Teflon lined autoclave and heated to 160°C for 24 h. Colorless crystals were harvested and air dried (Yield: 45 %). Elemental Analysis for calculated formula Zn₅(HTet)₆(Tet)₃(OH⁻)₇: C = 11.04 %(theo.: 10.08 %), H = 2.01 % (2.07 %), N = 45.94 % (47.02%).

Single Crystal X-ray Diffraction

Table 1: Crystal data and structure refinement

Empirical formula	C ₉ H ₉ N ₃₆ O ₇ Zn ₅
Formula weight	1060.37
Temperature	150(2) K
Wavelength	1.54178 Å
Crystal system, space group	Trigonal, P -3 1 c
Unit cell dimensions	a = 12.478(1) Å c = 12.708(1) Å
Volume	1713.6(5) Å ³
Z, Calculated density	2, 2.055
Absorption coefficient	4.741 mm ⁻¹
F(000)	1042
Crystal size	0.340 x 0.205 x 0.069 mm
Theta range for data collection	4.09° to 66.83°
Limiting indices	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -14 ≤ l ≤ 12
Reflections collected / unique	17668 / 969 [R(int) = 0.0542]
Completeness to theta = 66.83	94.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6451
Data / restraints / parameters	969 / 0 / 89
Goodness-of-fit on F ²	1.054
Final R indices [I > 2σ(I)]	R ₁ = 0.0729, wR ₂ = 0.2330
R indices (all data)	R ₁ = 0.0746, wR ₂ = 0.2367
Largest diff. peak and hole	1.860 and -2.248 e.Å ⁻³

WHAT IS CLAIMED IS:

1. A metal organic framework (MOF) composition, comprising:
 - one or more metal ions;
 - a plurality of organic ligands; and
 - a solvent;wherein the one or more metal ions associate with the plurality of organic ligands sufficient to form a MOF with kag topology.
2. The composition of claim 1, wherein the metal ions comprises one or more of Zn^{2+} , Cu^{2+} , Ni^{2+} , and Co^{2+} .
3. The composition of claim 1, wherein the ligands include N donor ligands.
4. The composition of claim 1, wherein the ligands comprise one or more of tetrazole, triazole, and derivatives of tetrazole and triazole.
5. The composition of claim 1, wherein a pore size of the MOF is about 3.4Å to 4.8Å.
6. The composition of claim 1, wherein the MOF composition is hydrothermally synthesized and highly stable.
7. The composition of claim 1, wherein the MOF composition crystallizes in the hexagonal space group P63/mmc.
8. A method of making a metal organic framework (MOF) composition, comprising:
 - contacting one or more metal ions with a plurality of organic ligands in the presence of a solvent, sufficient to form a MOF with kag topology,
 - wherein the solvent comprises water only.
9. The method of claim 8, wherein the metal ions comprises one or more of Zn^{2+} , Cu^{2+} , Ni^{2+} , and Co^{2+} .

10. The method of claim 8, wherein the ligands comprise N donor ligands.
11. The method of claim 8, wherein the ligands comprise one or more of tetrazole, triazole, and derivatives of tetrazole and triazole.
12. The method of claim 8, wherein a pore size of the MOF is about 3.4Å to 4.8Å.
13. The method of claim 8, wherein the MOF composition is hydrothermally synthesized and highly stable.
14. A method of capturing chemical species from a fluid composition, the method comprising
 contacting a metal organic framework (MOF) composition with kag topology and
 pore size of about 3.4Å to 4.8Å with a fluid composition comprising two
 or more chemical species; and
 capturing one or more captured chemical species from the fluid composition.
15. The method of claim 14, wherein the MOF composition includes one or more of Zn^{2+} , Cu^{2+} , Ni^{2+} , and Co^{2+} metal ions.
16. The method of claim 14, wherein the MOF composition includes a plurality of organic ligands.
17. The method of claim 16, wherein the ligands of the MOF composition includes N donor ligands.
18. The method of claim 16, wherein the ligands of the MOF composition include one or more of tetrazole, triazole and derivatives of tetrazole and triazole.
19. The method of claim 14, wherein capturing comprises physical adsorption of the one or more captured chemical species by the metal organic framework.
20. The method of claim 14, wherein the fluid composition comprises H_2S , and one or more of benzene, toluene, xylene, and the one or more captured chemical species consists of H_2S .

21. The method of claim 14, wherein the one or more captured chemical species consists of carbon dioxide.
22. The method of claim 14, wherein the fluid composition comprises one or more of natural gas, flue gas, syngas, biogas and landfill gas, and the captured chemical species consists of carbon dioxide.
23. The method of claim 14, wherein the fluid composition comprises water and one or more of a gas, a vapor, and a solvent, and the captured chemical species consists of water.
24. The method of claim 14, wherein the fluid composition comprises two or more of acetone, phenol, and C₄ fractions, and the one or more captured chemical species consists of acetone.
25. The method of claim 14, wherein the MOF composition is used as a separation agent in a pressure-temperature swing system.

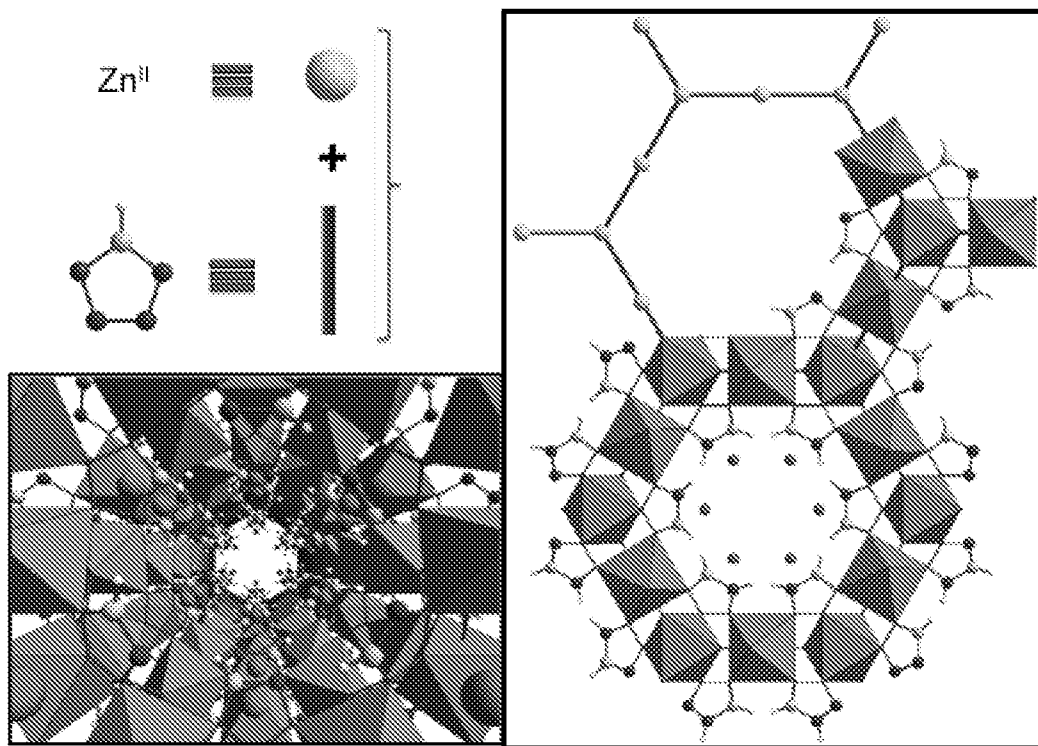


FIGURE 1

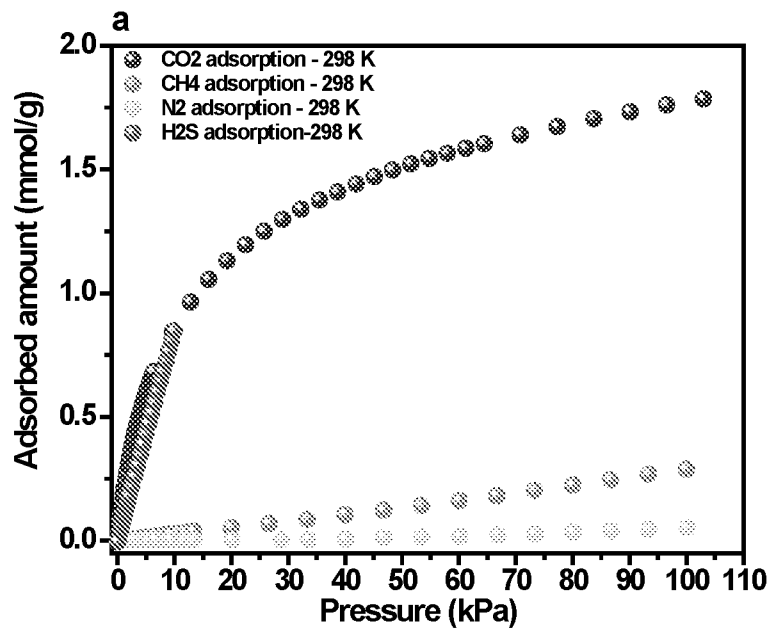
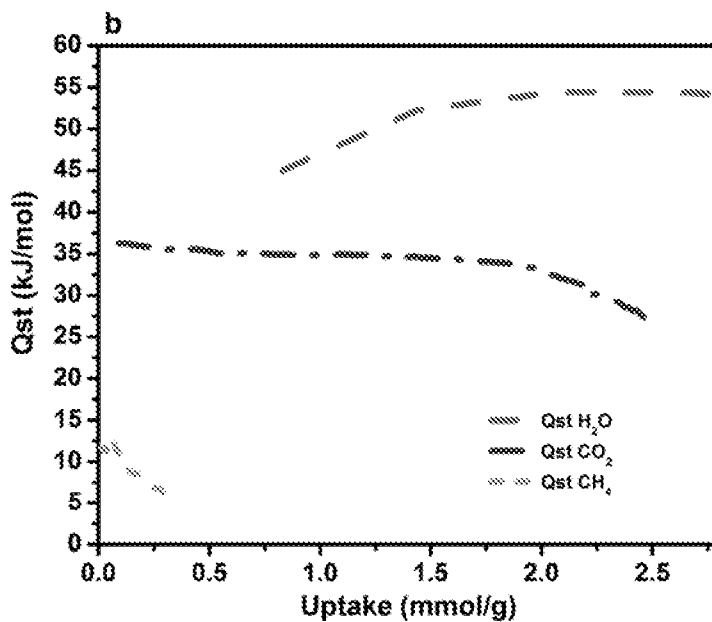


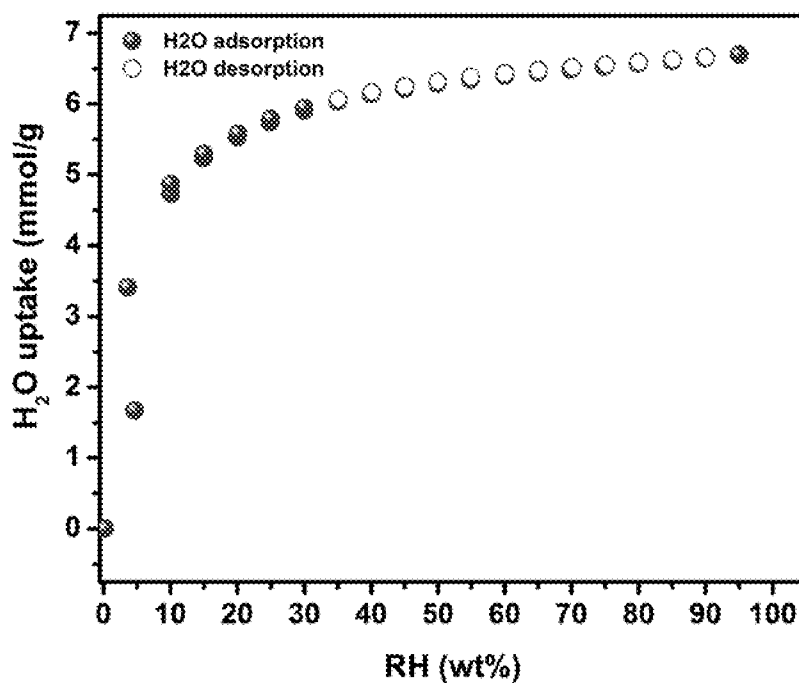
FIGURE 2A

FIGURE 2B



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FIGURE 3



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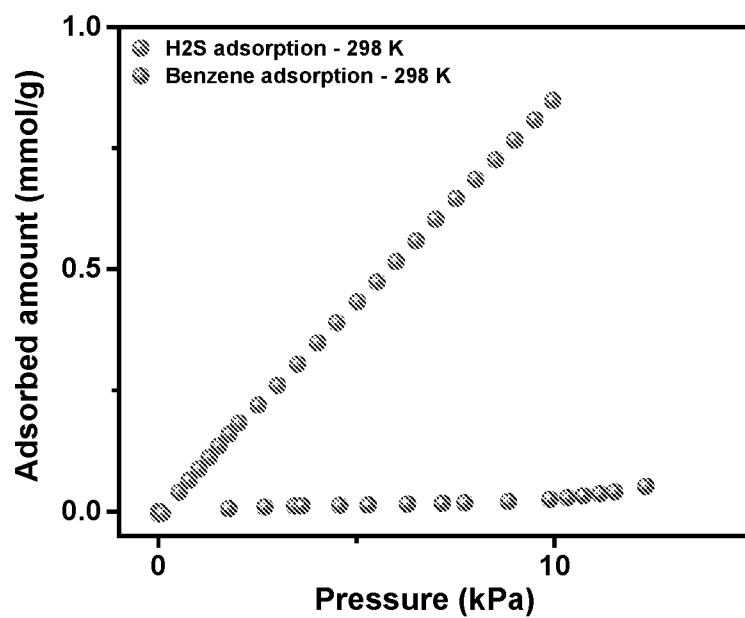
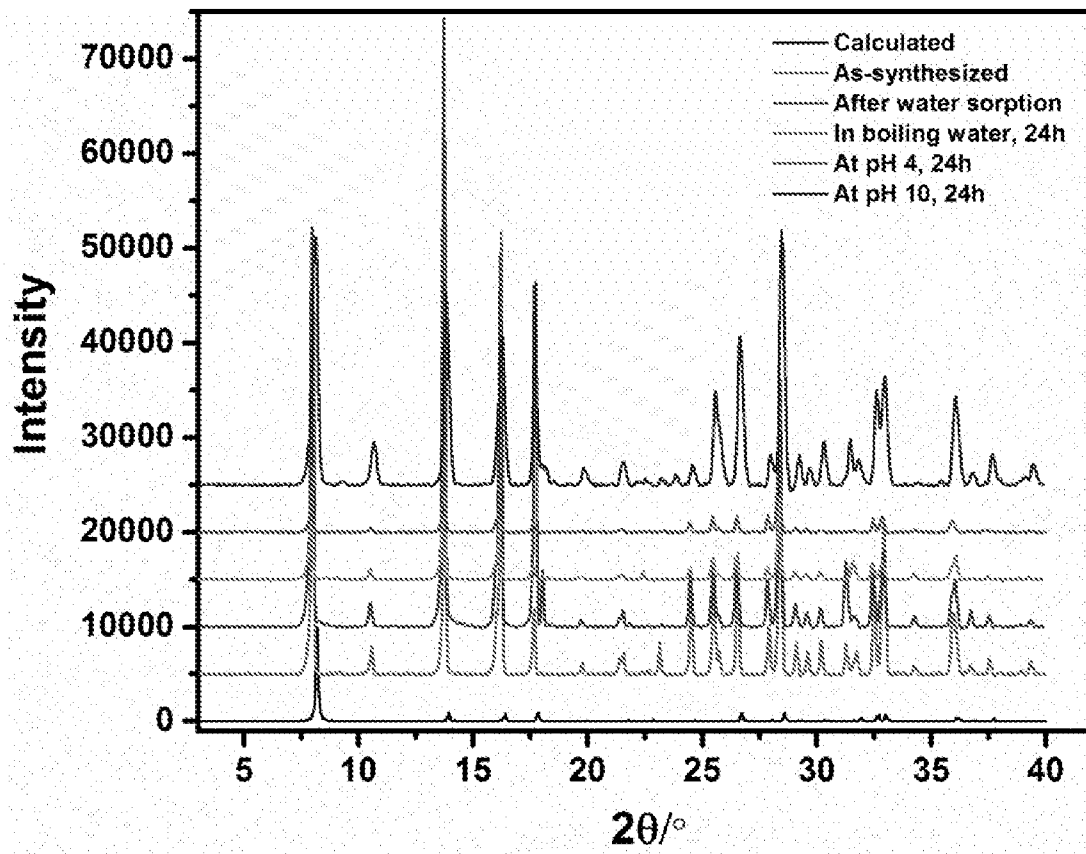


FIGURE 4

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FIGURE 5



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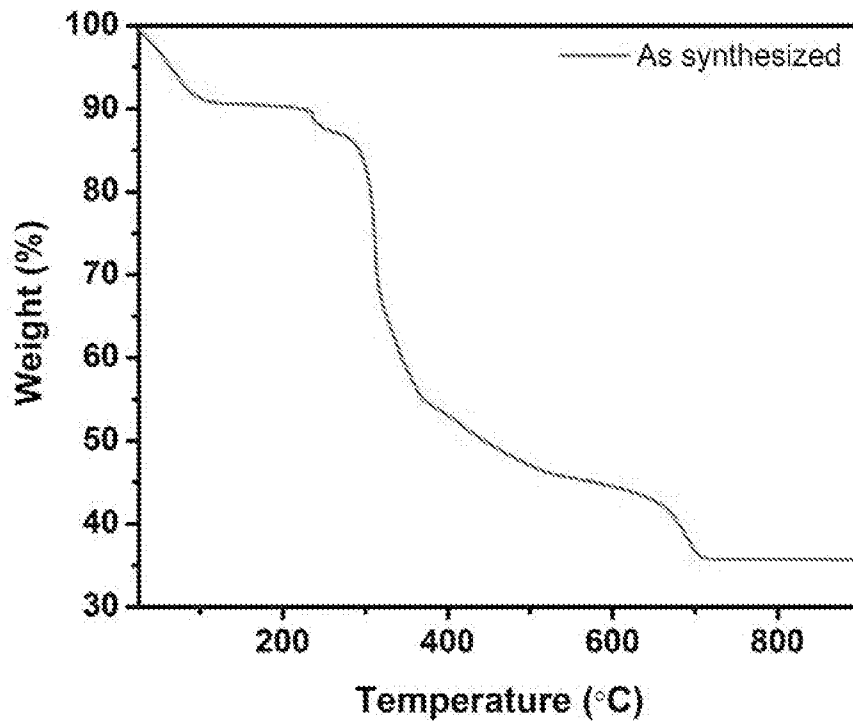


FIGURE 6

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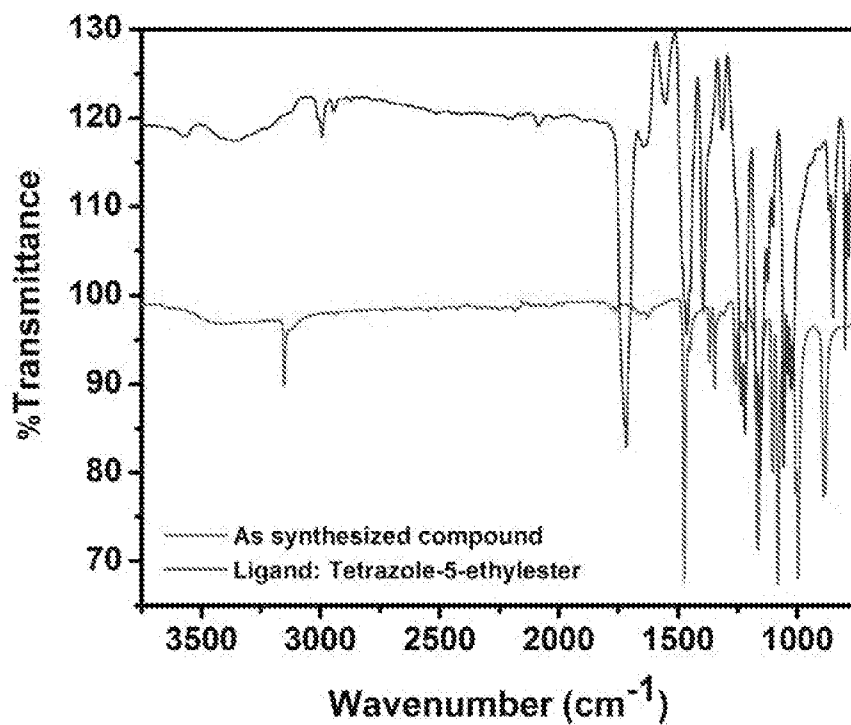
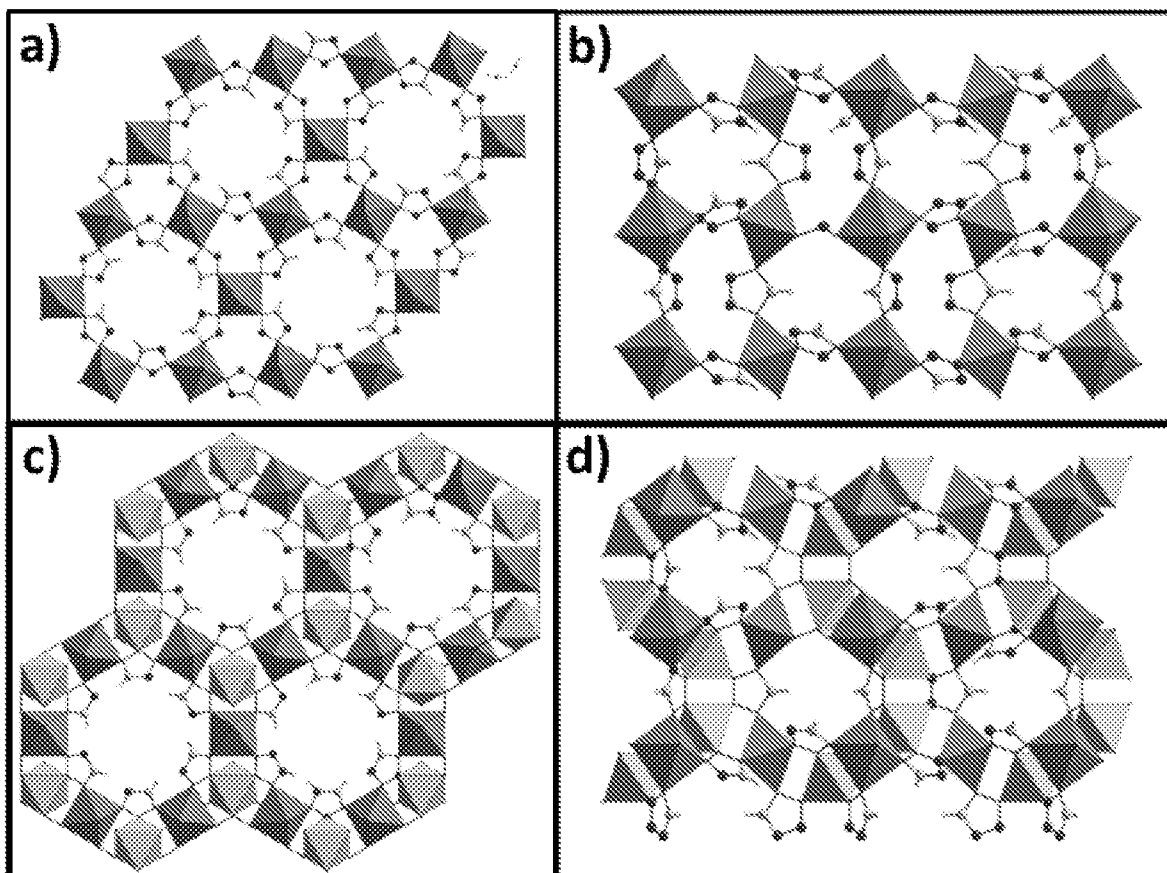


FIGURE 7

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FIGURES 8A-D



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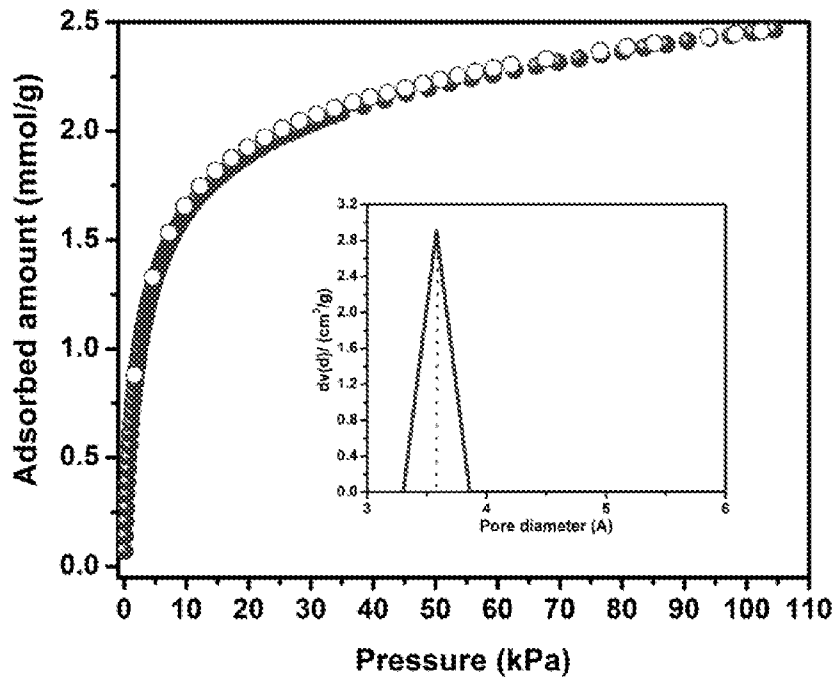
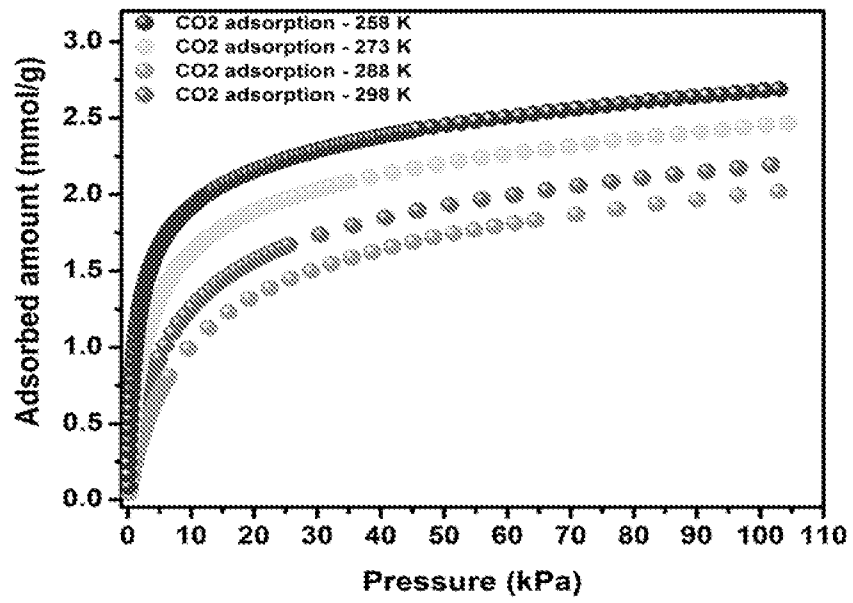


FIGURE 9

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FIGURE 10



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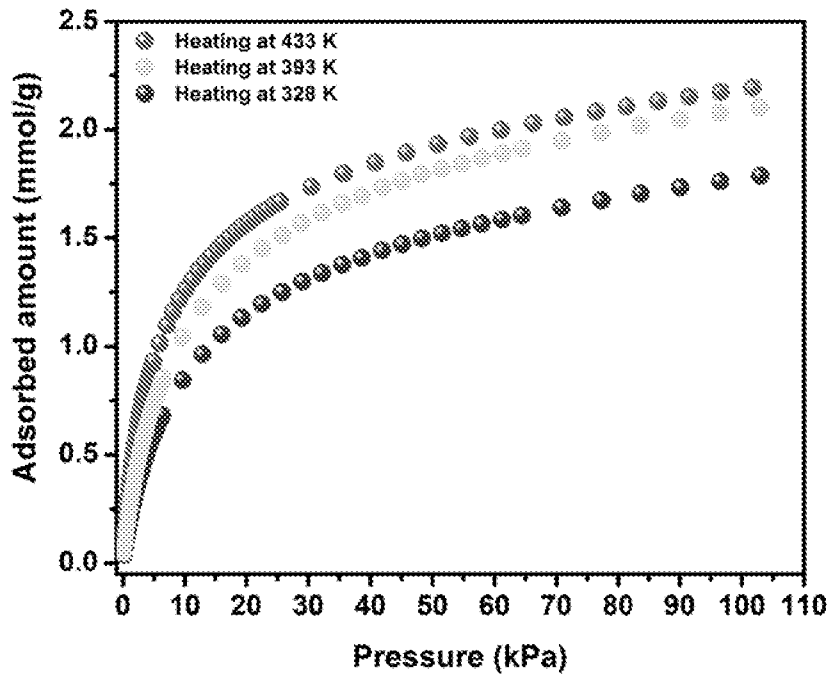
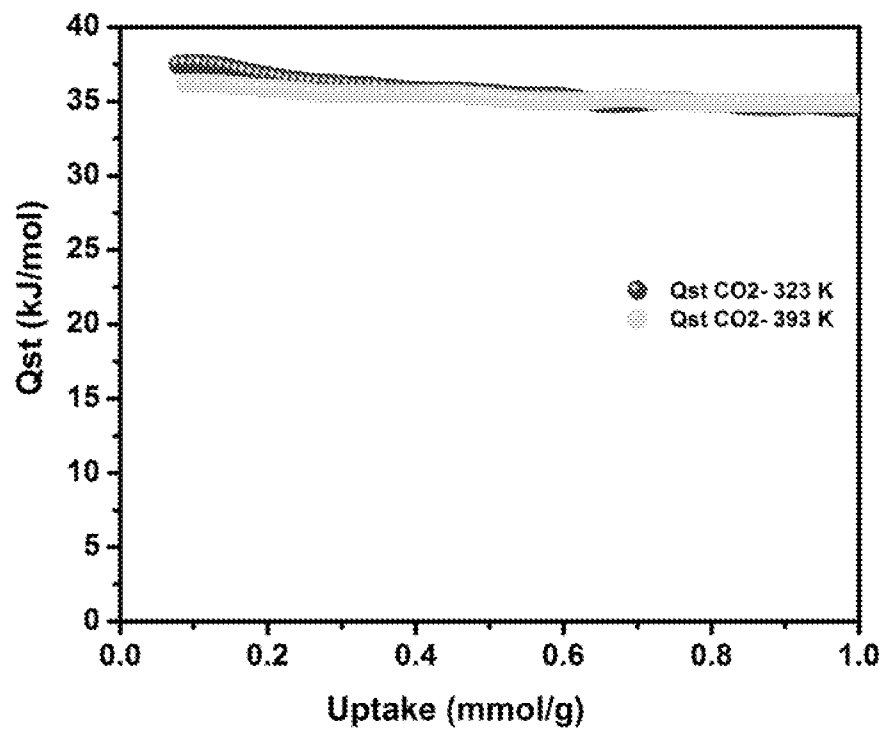


FIGURE 11

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FIGURE 12



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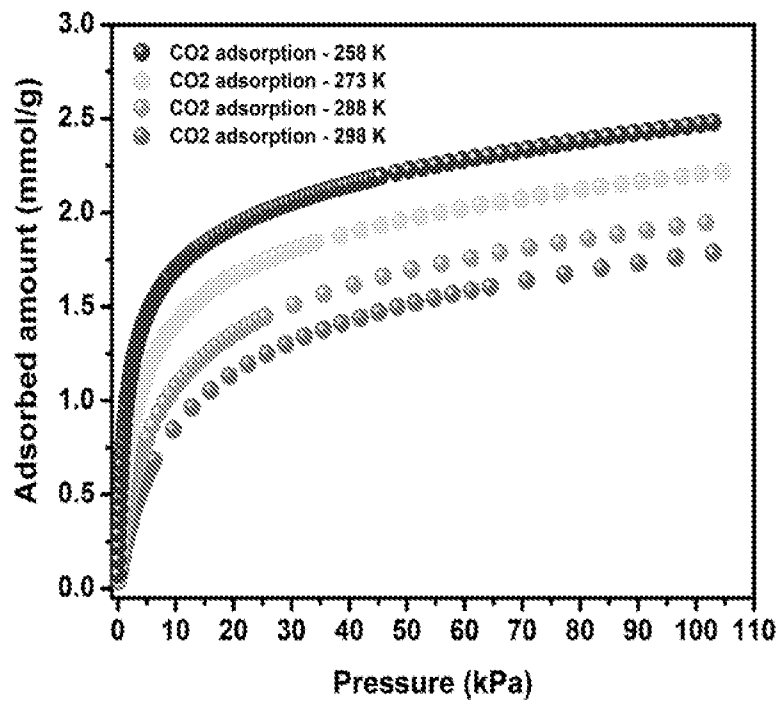
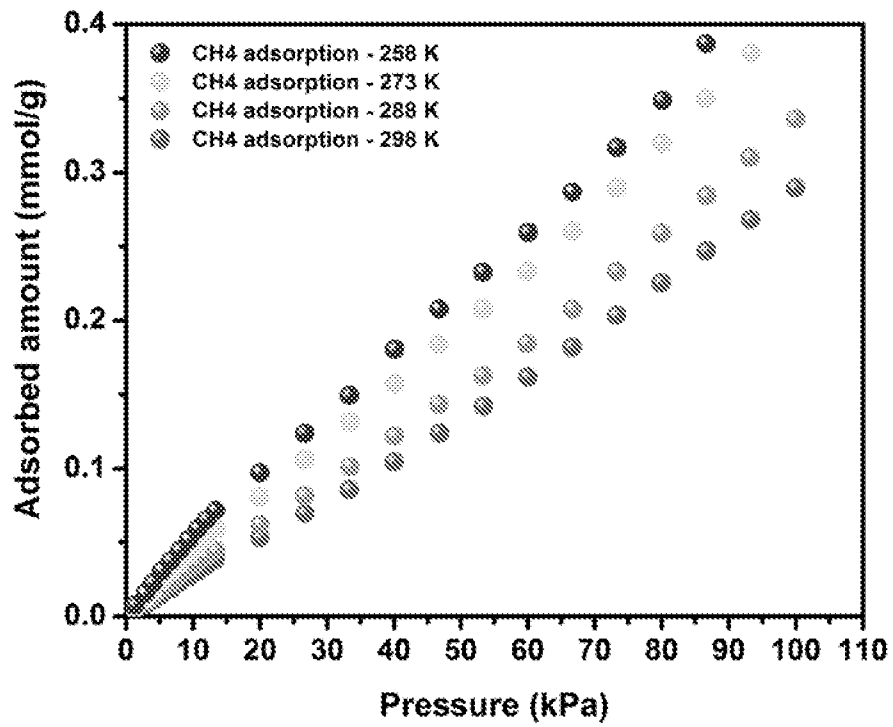


FIGURE 13

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FIGURE 14



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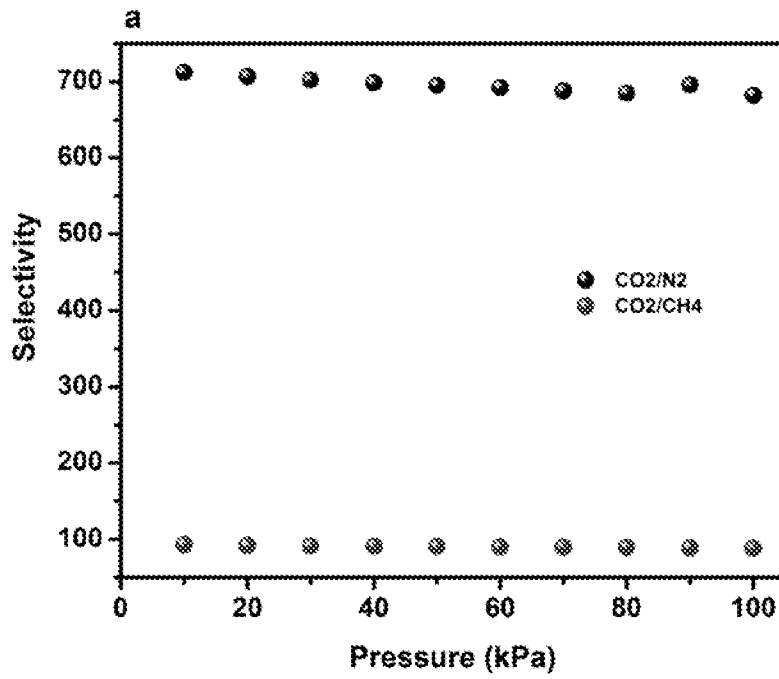
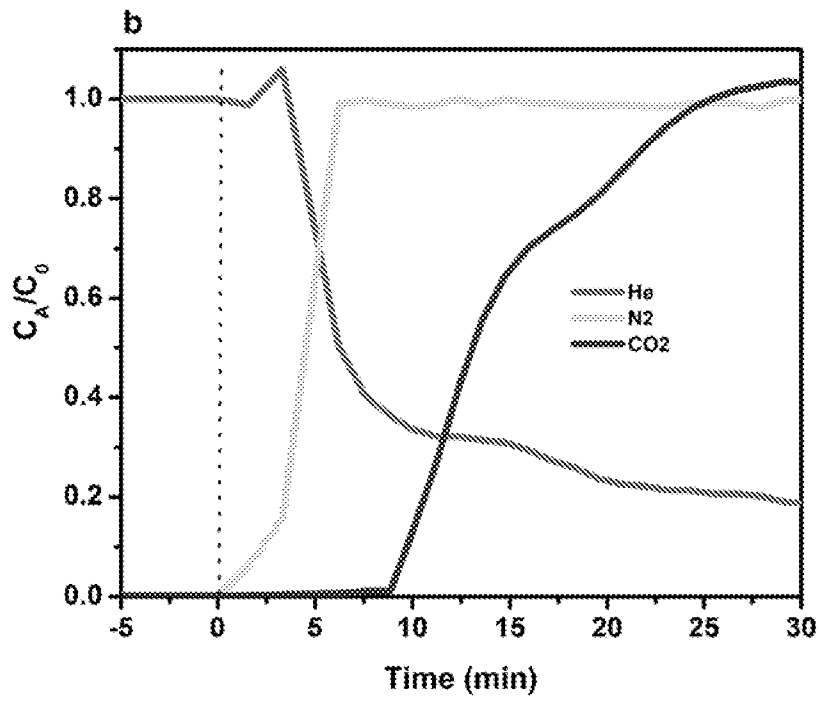


FIGURE 15A

FIGURE 15B



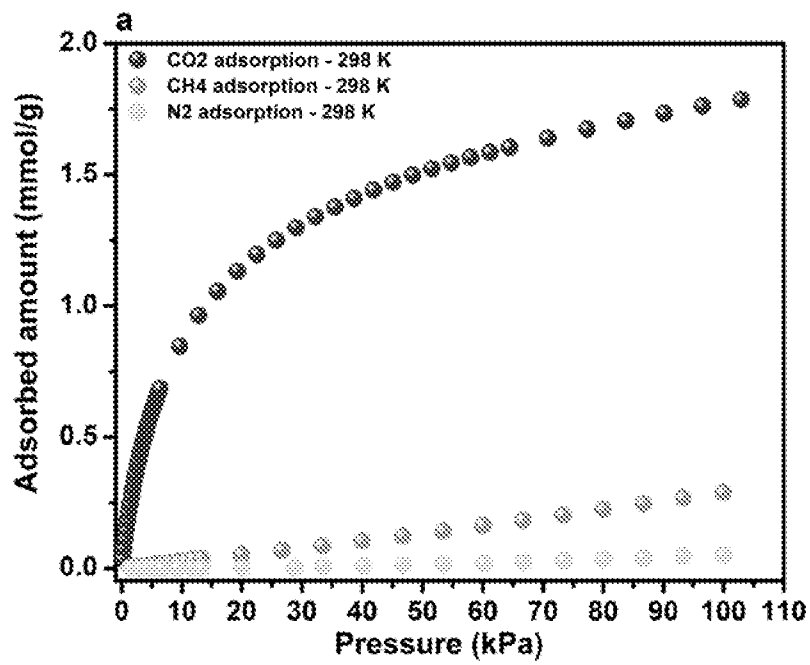
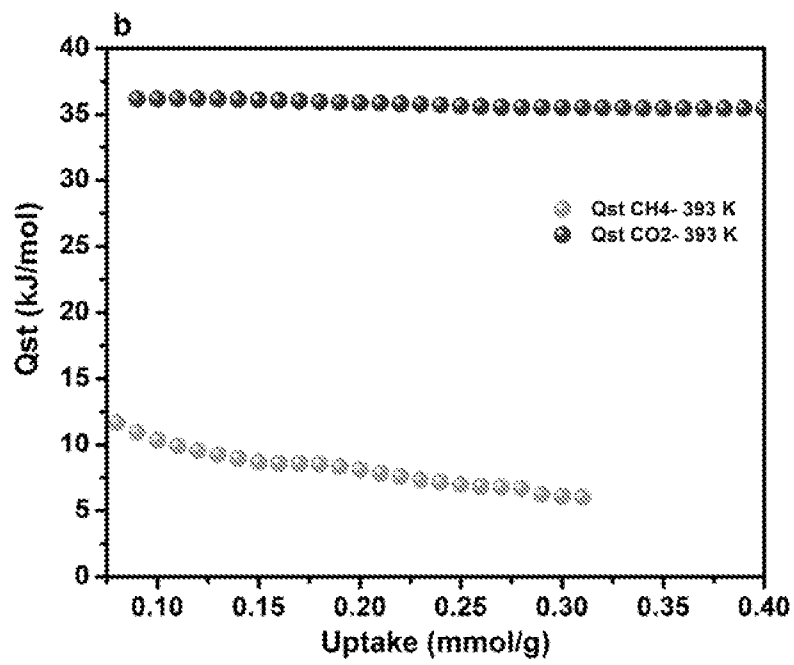


FIGURE 16A

FIGURE 16B



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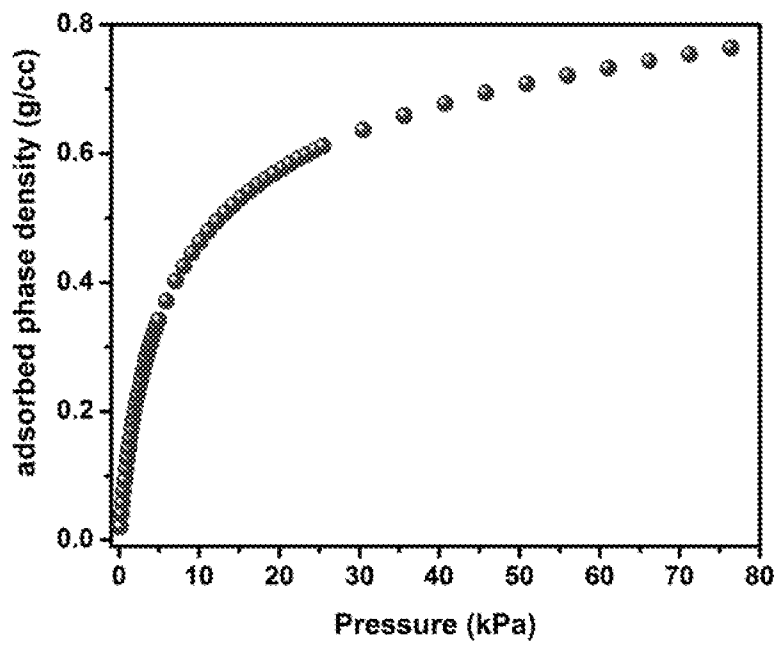


FIGURE 17

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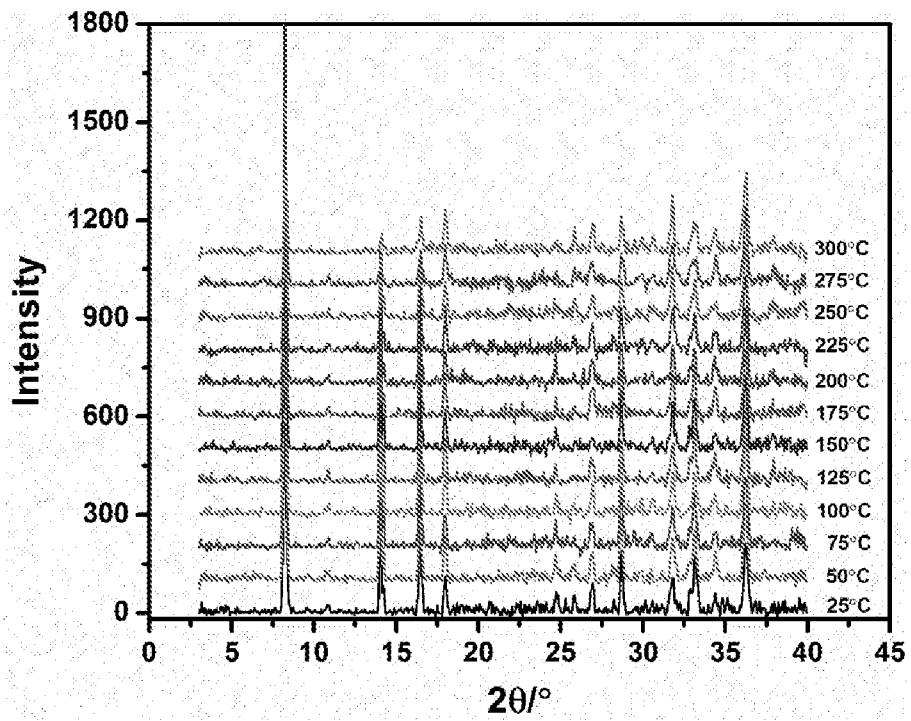
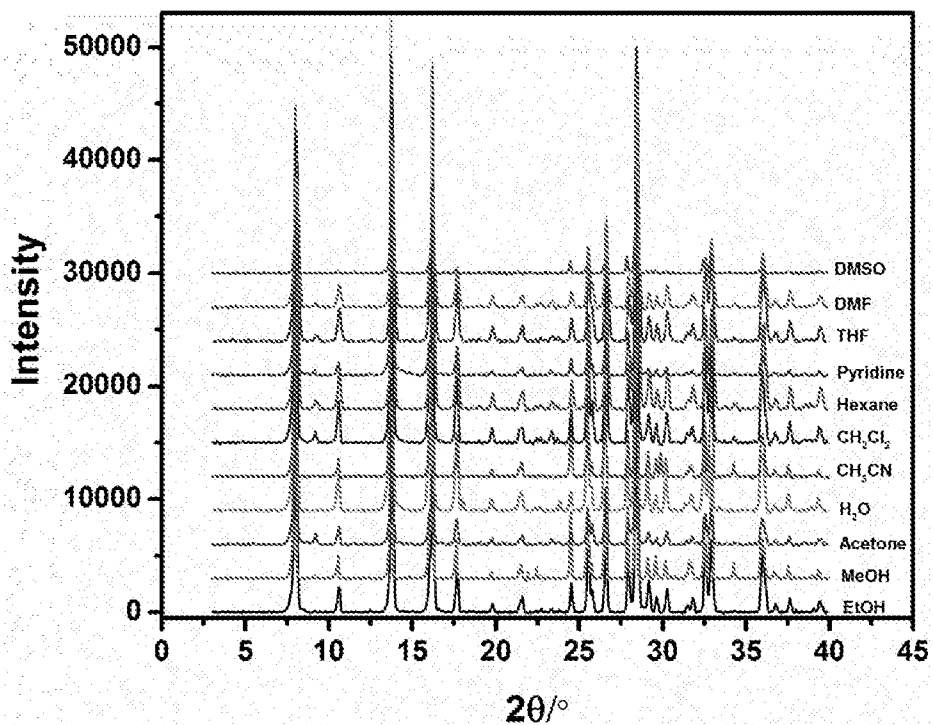


FIGURE 18

FIGURE 19



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/056435

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01J20/22 B01J20/28 B01J20/30 B01D53/04
 ADD.
 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)
 B01J B01D
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LI DONG-SHENG ET AL: "Metal-organic frameworks based upon non-zeotype 4-connected topology", COORDINATION CHEMISTRY REVIEWS, vol. 261, 15 February 2014 (2014-02-15), pages 1-27, XP028801980, ISSN: 0010-8545, DOI: 10.1016/J.CCR.2013.11.004 3.2. kag-type MOFs; page 7, right-hand column - page 8, left-hand column figures 2,3 ----- -/--	1-7

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 another 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
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Date of the actual completion of the international search 22 December 2016	Date of mailing of the international search report 10/01/2017
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kaluza, Nicoleta
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DI-CHANG ZHONG ET AL: "Three Coordination Polymers Based on 1 H -Tetrazole (HTz) Generated via in Situ Decarboxylation: Synthesis, Structures, and Selective Gas Adsorption Properties", CRYSTAL GROWTH & DESIGN., vol. 10, no. 2, 3 February 2010 (2010-02-03), pages 739-746, XP055331270, US ISSN: 1528-7483, DOI: 10.1021/cg901128k abstract Experimental section; page 739, right-hand column - page 740, left-hand column figure 7</p>	1-7, 14-25
X	<p>WEI-XIONG ZHANG ET AL: "Flexible Mixed-Spin Kagomé Coordination Polymers with Reversible Magnetism Triggered by Dehydration and Rehydration", INORGANIC CHEMISTRY, vol. 50, no. 1, 3 January 2011 (2011-01-03), pages 309-316, XP055331277, EASTON, US ISSN: 0020-1669, DOI: 10.1021/ic101948q abstract scheme 1; page 310 Experimental Section; page 310, right-hand column - page 311, left-hand column pages 1,2; figures 1,2</p>	1-13
A	<p>PING CUI ET AL: "Multipoint Interactions Enhanced CO₂ Uptake: A Zeolite-like Zinc-Tetrazole Framework with 24-Nuclear Zinc Cages", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 134, no. 46, 21 November 2012 (2012-11-21), pages 18892-18895, XP055331273, US ISSN: 0002-7863, DOI: 10.1021/ja3063138 the whole document</p>	1-25