(51) International Patent Classification:
C10G 25/00 (2006.01) B01J 20/22 (2006.01)

(21) International Application Number:
PCT/IB2016/056144

(22) International Filing Date:
13 October 2016 (13.10.2016)

(25) Filing Language:
English

(26) Publication Language:
English

(30) Priority Data:

(71) Applicant: KING ABDULLAH UNIVERSITY OF SCIENCE AND TECHNOLOGY [SA/SA]; 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900 (SA).

(72) Inventors: EDDAOUDI, Mohamed; 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900 (SA). MOHIDEEN, Mohamad Infas Haja; 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900 (SA).


(54) Title: ZEOLITE-LIKE METAL-ORGANIC FRAMEWORKS WITH ANA TOPOLOGY

(57) Abstract: Embodiments of the present disclosure describe a zeolite-like metal-organic framework composition comprising a metal-organic framework composition with an ana topology characterized by the formula [M^n(4,5-imidazole dicarboxylic acid)]_x(solvent)_y, wherein M^n comprises a trivalent cation of a rare earth element, X comprises an alkali metal element or alkaline earth metal element, and solvent comprises a guest molecule occupying pores. Embodiments of the present disclosure describe a method of separating paraffins comprising contacting a zeolite-like metal-organic framework with an ana topology with a flow of paraffins, and separating the paraffins by size.
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.


Declarations under Rule 4.17:
— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:
— with international search report (Art. 21(3))
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))
ZEOLITE-LIKE METAL-ORGANIC FRAMEWORKS WITH ANA TOPOLOGY

BACKGROUND

[0001] The oil and gas industries separate linear paraffins from branched paraffins to aid in the production of high quality fuels. For instance, gasoline with a high octane rating results in less engine knocking in internal combustion engines and improved engine performance. Diesel engines, on the other hand, perform optimally with high cetane fuel, which readily ignites under pressures typically observed in a diesel engine. Separating paraffins is important to these industries because the octane rating and cetane rating are directly related to the amount of linear paraffins and branched paraffins present in the fuel. Now that reducing harmful emissions is a matter of global concern, processes that separate linear paraffins from branched paraffins have become increasingly important.

[0002] The separation of linear paraffins from branched paraffins, however, remains one of the most intensive and challenging separations of today. Fractionation or distillation processes are employed to separate paraffins, but these processes consume large amounts of energy. Adsorption through zeolite molecular sieves processes are also employed to accomplish the separation, but these processes are less efficient as 3% to 4% of branched paraffins diffuse and/or adsorb on the adsorbent. Metal-organic frameworks offer great potential as an adsorbent or membrane, given the ability to tune or control pore aperture and the potential to alter adsorption and diffusion properties via cation exchange. However, to date, there have been no reports of achieving a complete separation of linear paraffins from branched paraffins using a metal-organic framework.

SUMMARY OF THE INVENTION

[0003] In general, this disclosure describes embodiments relating to a zeolite-like metal-organic framework with ana topology. More specifically, this disclosure describes a zeolite-like metal-organic framework with ana topology that may be used to kinetically separate paraffins.

[0004] Embodiments of the present disclosure describe a zeolite-like metal-organic framework composition comprising a metal-organic framework composition with ana topology characterized by the formula \( [M^{III}(4, 5\text{-imidazole dicarboxylic acid})_2X(\text{solvent})_3]_n \) wherein \( M^{III} \) comprises a trivalent cation of a rare earth element, \( X \) comprises an alkali metal element or alkaline earth metal element, and solvent comprises a guest molecule occupying pores.
[0005] Embodiments of the present disclosure describe a method of separating paraffins comprising contacting a zeolite-like metal-organic framework with ana topology with a flow of paraffins, and separating the paraffins by size.

[0006] The details of one or more examples are set forth in the accompanying drawings and the description below. Other features, objects, and advantages will be apparent from the description and drawings, and from the claims.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0007] The accompanying drawings illustrate non-limiting example embodiments of the invention.

[0008] FIG. 1 illustrates a schematic view of a zeolite-like metal-organic framework with ana topology, according to some embodiments.

[0009] FIG. 2 illustrates a graphical view of single-component adsorption isotherms for pentane, isopentane, and 2,2,4-trimethylpentane on a zeolite-like metal-organic framework with ana topology, indicating the amount of pentane, isopentane, and 2,2,4-trimethylpentane adsorbed with changes in pressure at 20°C, according to some embodiments.

[0010] FIG. 3 illustrates a graphical view of the adsorption of pentane and isopentane on a zeolite-like metal-organic framework with ana topology, indicating the normalized pressure of pentane and isopentane as a function of time at 20°C, according to some embodiments.

[0011] FIG. 4 illustrates a scanning electron microscopy image with a view from the top of a zeolite-like metal-organic framework with ana topology membrane fabricated on alumina substrate, according to some embodiments.

[0012] FIG. 5 illustrates a scanning electron microscopy image with a view of the cross-section of a zeolite-like metal-organic framework with ana topology membrane fabricated on alumina substrate, according to some embodiments.

[0013] FIG. 6 illustrates a representation of gasoline through a schematic view of isomers of hexane with their corresponding kinetic diameters and Research Octane Numbers (RON), according to some embodiments.

[0014] FIG. 7 illustrates a representation of the components of diesel fuel through a schematic view of paraffins with their corresponding kinetic diameters and Research Octane Numbers (RON), according to some embodiments.

**DETAILED DESCRIPTION**

[0015] The present invention relates to a microporous zeolite-like metal-organic framework with ana topology (ana-ZMOF) that can be used as a kinetic-base adsorbent to
separate paraffins by size. The disclosure herein provides compositions of ana-ZMOF and methods of separating paraffins using an ana-ZMOF. The ana-ZMOF described herein can be used as a kinetic-based adsorbent to about completely separate paraffins by size. The ana-ZMOF can be fabricated as a molecular sieve or as a thin-film membrane. The adsorption and diffusion properties of ana-ZMOF, which is anionic, can be altered or modified through cation exchange. The pore aperture sizes of the ana-ZMOF disclosed herein can be tuned to within a difference of less than about 0.5 Angstroms (Å). Embodiments provided herein describe a chemical formula of an ana-ZMOF. Embodiments further describe a method of separating paraffins by size using an ana-ZMOF. Embodiments further describe an ana-ZMOF used as a kinetics-based adsorbent for kinetic sieving of linear paraffins from branched paraffins involving molecules with a kinetics diameter of greater than about 4.2Å. Embodiments provided herein describe employing ana-ZMOF as an adsorbent to achieve a full sieving of di-branched paraffins and tri-branched paraffins. Embodiments provided herein describe employing ana-ZMOF as an adsorbent to separate pentane from iso-pentane. Embodiments provided herein also describe employing ana-ZMOF as an adsorbent to achieve about a full sieving of 2,2,4-trimethylpentane. Embodiments describe employing ana-ZMOF as a molecular sieve to separate high octane rating paraffins from low octane rating mono-branched paraffins and linear paraffins with infinite selectivity. Numerous other advantages and uses of an ana-ZMOF will be readily apparent to one of skill in the art.

[0016] The figures referenced in the description of the many embodiments of this disclosure are not necessarily drawn to scale and they are provided merely to illustrate the invention. Several aspects of the invention are described below with reference to example applications for illustration. It should be understood that numerous specific details, relationships, and methods are set forth to provide an understanding of the invention. One skilled in the relevant art, however, will readily recognize that the invention can be practiced without one or more of the specific details or with other methods. In other instances, well-known structures or operations are not shown in detail to avoid obscuring the invention. The present invention is not limited by the illustrated ordering of acts or events, as some acts may occur in different orders and/or concurrently with other acts or events. Furthermore, not all illustrated acts or events are required to implement a methodology in accordance with the present invention.

[0017] Many terms used herein are defined below. Other terms not expressly defined should be read in the context of this specification before being given their ordinary meanings as understood by one of skill in the art.
As used herein, “rare earth element” refers to cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lutetium, neodymium, praseodymium, promethium, samarium, scandium, terbium, thulium, ytterbium, or yttrium.

As used herein, “alkali metal element” refers to lithium, sodium, potassium, rubidium, caesium, or francium.

As used herein, “alkaline earth metal element” refers to beryllium, magnesium, calcium, strontium, barium, or radium.

As used herein, “paraffin” refers to CₙH₂n₊₂, wherein n- as a prefix refers to a linear paraffin and iso- as a prefix refers to a branched paraffin.

Zeolites are purely inorganic crystalline microporous materials of commercial significance. A defining feature of zeolites is a three-dimensional framework comprised of Si and/or Al tetrahedral metal ions linked by oxide ions at a pre-defined angle. These tetrahedra link to form a variety of structures with regular intra-crystalline cavities and channels of molecular dimensions, and bear a net negative charge that is balanced by an extra-framework cation. As a size-selective adsorbent, zeolites are employed as molecule sieves or membranes to achieve separations through a difference in molecular diameter and pore aperture, where molecules with a diameter less than the pore aperture diameter adsorb and/or diffuse through the adsorbent, leaving any molecules with diameters greater than the pore diameter in the bulk phase.

Zeolites have been particularly effective as molecular sieves to separate linear hydrocarbons, such as n-butane and n-pentane, from branched hydrocarbons, such as iso-butane and iso-pentane. The ongoing challenge with zeolites, however, is the inability to tune pore size with greater precision to achieve more efficient separations. For instance, Zeolite 5A, with a pore aperture of 4.2 Å, does not achieve a full sieving of linear paraffins, as about 3% to 4% of the valuable branched paraffins are lost due to diffusion and adsorption on the adsorbent. Despite the maturity of zeolite chemistry, zeolite technology has not allowed tuning of pore size in the range lower than 1 Å difference in pore aperture size. For example, existing zeolite molecular sieves are characterized as 3 Å, 4 Å, and 5 Å.

Metal-organic frameworks (MOF), on the other hand, have exhibited much more control over pore size than zeolites. For instance, MOFs exhibit control of pore size to within a range of less than 0.5 Å in difference. A MOF is a crystalline material that combines ligands and metal ions or metal clusters to form one-, two-, and three-dimensional networked structures with large surface areas that can be porous. While the tunable pore size, structure, functionality, and properties of MOFs make them attractive for a variety of applications, including, among other
things, gas separations, only a few examples of MOFs exhibiting kinetic-based gas separations have been reported. Moreover, almost no examples of using MOFs to achieve a full sieving in gas separations at 298K have been reported.

[0025] Metal-organic frameworks with zeolite-like topologies, or ZMOFs, have shown great promise for kinetic-based and gas sieving separation processes in bulk adsorbent and membrane forms. The topologies of ZMOFs are isomorphic with zeolites. ZMOFs exhibit properties such as tunable pore sizes and cavities, chemical stability, and the ability to control and tune extra-framework cations via ion exchange. ZMOFs are constructed from a single-metal-ion-based molecular building block (MBB) that can be produced in situ from single metal ions heterochelated by multifunctional ligands. ZMOFs have been described, for example, in U.S. Patent No. 8,415,493, which is hereby incorporated by reference in its entirety.

[0026] The present invention relates to a zeolite-like metal-organic framework with ana topology (ana-ZMOF) and its use as a material for separating paraffins. See Figure 1, for example, which is a schematic view of a zeolite-like metal-organic framework with ana topology, according to some embodiments.

[0027] The composition of the ana-ZMOF is characterized by the formula \[\text{[M}^{III}(4,5-\text{imidazole dica}}\text{rboxylic acid})_2\text{X(solvent)}_n\], wherein \(n\) represents the number of molecular building blocks.

[0028] In some embodiments, \(\text{M}^{III}\) comprises one or more of a trivalent cation of a rare earth element, including cerium (Ce\(^{3+}\)), dysprosium (Dy\(^{3+}\)), erbium (Er\(^{3+}\)), europium (Eu\(^{3+}\)), gadolinium (Gd\(^{3+}\)), holmium (Ho\(^{3+}\)), lanthanum (La\(^{3+}\)), lutetium (Lu\(^{3+}\)), neodymium (Nd\(^{3+}\)), praseodymium (Pr\(^{3+}\)), promethium (Pm\(^{3+}\)), samarium (Sm\(^{3+}\)), scandium (Sc\(^{3+}\)), terbium (Tb\(^{3+}\)), thulium (Tm\(^{3+}\)), ytterbium (Yb\(^{3+}\)), or yttrium (Y\(^{3+}\)).

[0029] In some embodiments, the ligand is a heterofunctional ditopic ligand, such as 4,5-imidazole dicarboxylic acid (ImDC). ImDC possesses two \(N\)- and \(O\)-hetero-chelating moieties with a potential angle of 144°, as directed by the metal-nitrogen coordination. In some embodiments the ligand is one or more of 1H-Imidazole-2-carboxylic acid, pyrimidine-4,6-dicarboxylic acid, and pyridine-2,5-dicarboxylic acid. Different properties may be observed with slight variations in the bulky character of a ligand and in a ligand’s size (e.g., length).

[0030] In some embodiments, X comprises one or more of an alkali metal element, including lithium, sodium, potassium, rubidium, cesium, or francium. In other embodiments, X comprises one or more of an alkaline earth metal element, including beryllium, magnesium, calcium, strontium, barium, or radium.
[0031] A solvent comprises a guest molecule that, as a result of synthesis, occupies pores of the ana-ZMOF. In some embodiments, the solvent can be H₂O, N,N-dimethyl formamide (DMF), ethanol, 4,4'-trimethylene-dipiperidine, or 1,2-diaminocyclohexane. In other embodiments, the solvent guest molecules are evacuated. Consequently, a can vary down to zero, without any change in the definitional framework of the ana-ZMOF.

[0032] An ana topology is characterized by a M⁺⁺⁺ cation connected to four organic linkers in a tetrahedral arrangement. These tetrahedral units connect to form four- and six-membered rings that delimit a three-dimensional channel system with distorted eight-membered ring openings.

[0033] The ana-ZMOF disclosed herein can be used to separate paraffins. In some embodiments, the ana-ZMOF may be used to separate paraffins by size. In other embodiments, the ana-ZMOF may be used to separate paraffins based on a degree of branching. In some embodiments, the ana-ZMOF may be used to separate isoparaffins from paraffins. In other embodiments, the ana-ZMOF may be used to separate linear paraffins from branched paraffins. Single component adsorption isotherms of linear paraffins and branched paraffins illustrate that the adsorption of linear paraffins is nearly double the adsorption of branched paraffins. In addition, an analysis of the kinetics of sorption on ana-ZMOF shows that linear paraffins are adsorbed at a much faster rate than branched paraffins. Consequently, ana-ZMOF is the ideal candidate material for kinetically separating linear paraffins from branched paraffins.

[0034] In some embodiments, the separation is kinetically driven. For example, in some embodiments, the separation of linear paraffins from branched paraffins is kinetic-based, as opposed to equilibrium-based. In some embodiments, the separation is based on a difference in kinetic diameter and pore aperture size, wherein paraffins with a kinetic diameter that is less than the pore aperture diameter diffuse and/or adsorb on the ana-ZMOF and paraffins with a kinetic diameter that is greater than the pore aperture diameter remain in the bulk phase. In some embodiments, ana-ZMOF is used to separate paraffins with a kinetics diameter greater than about 4.2Å to about 5Å. In some embodiments, the separation is based on a difference in time that it takes a paraffin to reach equilibrium for sorption on an ana-ZMOF, wherein the time it takes a branched paraffin to reach equilibrium is much greater than the time it takes a linear paraffin to do the same. In some embodiments, the separation is based on both a difference in kinetic diameter and/or pore size, and a difference in equilibrium times.

[0035] A method of separating paraffins comprises contacting a zeolite-like metal-organic framework with ana topology with a flow of paraffins, and kinetically and completely separating paraffins by size and/or based on a degree of branching. In some embodiments, ana-
ZMOF is used to separate isoparaffins from paraffins. In some embodiments, ana-ZMOF is used to separate linear paraffins from branched paraffins. In some embodiments, ana-ZMOF is used to separate linear paraffins from mono-branched paraffins, di-branched paraffins, tri-branched paraffins, cyclic paraffins, and other more highly branched paraffins. In some embodiments, ana-ZMOF is used to separate one or more of linear paraffins and mono-branched paraffins from one or more of di-branched paraffins, tri-branched paraffins, cyclic paraffins, and other more highly branched paraffins. In some embodiments, ana-ZMOF is used to separate paraffins with a high octave rating from paraffins with a low octave rating. In some embodiments, ana-ZMOF is used to separate paraffins with a high cetane rating from paraffins with a low cetane rating.

[0036] In some embodiments, ana-ZMOF is used as a kinetic-based adsorbent to separate linear paraffins from branched paraffins, wherein the separation involves molecules with a kinetics diameter of greater than about 4.2Å to about 5Å.

[0037] In some embodiments, ana-ZMOF is used to achieve a full sieving or a complete separation of linear paraffins from branched paraffins, resulting in an efficient separation of paraffins. In some embodiments, ana-ZMOF achieves a full sieving of di-branched paraffins. In some embodiments, ana-ZMOF achieves a full sieving of tri-branched paraffins.

[0038] The ana-ZMOF can be used as a kinetic-based adsorbent to kinetically separate pentane from isopentane. Figure 2 illustrates a graphical view of single-component adsorption isotherms for pentane, isopentane, and 2,2,4-trimethylpentane on a zeolite-like metal-organic framework with ana topology, indicating the amount of pentane, isopentane, and 2,2,4-trimethylpentane adsorbed with changes in pressure at 20°C. With respect to the separation of n-pentane from isopentane, Figure 2 illustrates that the adsorption of pentane on an ana-ZMOF is almost double the adsorption of isopentane. With respect to 2,2,4-trimethylpentane, Figure 2 illustrates that 2,2,4-trimethylpentane was experimentally not observed adsorbing onto or diffusing into the pores of ana-ZMOF. In some embodiments, ana-ZMOF can be used as a molecular sieve to separate high octane rating gasoline components from low octane rating gasoline components comprising mono-branched paraffins and linear paraffins, with infinite selectivity.

[0039] Figure 3 illustrates a graphical view of the adsorption of pentane and isopentane on a zeolite-like metal-organic framework with ana topology, indicating the normalized pressure of pentane and isopentane as a function of time at 20°C. More specifically, Figure 3 illustrates that an analysis of the kinetics of sorption clearly show that pentane is adsorbed much faster than isopentane, with a time of greater than 5000 seconds for the sorption of isopentane to reach equilibrium.
[0040] The ana-ZMOF disclosed herein is anionic. The adsorption and/or diffusion properties of an ana-ZMOF can be altered and/or modified through cation exchange. In some embodiments, the pore size or pore aperture of an ana-ZMOF is tuned via cation exchange. In some embodiments, pore size is tuned through cation exchange with an alkali metal ion or alkaline earth metal ion. In some embodiments, the pore size of an ana-ZMOF is tuned to within a range that is less than about 1 Å in difference. In some embodiments, the pore size of an ana-ZMOF is tuned to about 4.2 Å to 5 Å. In some embodiments, the pore size of an ana-ZMOF is tuned to within a range of less than about 0.5 Å in difference.

[0041] The ana-ZMOF disclosed herein can be used as a molecular sieve adsorbent or as a thin-film membrane. In some embodiments, ana-ZMOF is used as a molecular sieve adsorbent to separate linear paraffins from branched paraffins. In some embodiments, ana-ZMOF is used as a thin-film membrane to separate linear paraffins from branched paraffins. In some embodiments, a thin-film membrane comprising ana-ZMOF is fabricated on a support, such as a porous ceramic substrate. In some embodiments, a thin-film membrane comprising ana-ZMOF is fabricated on an alumina substrate.

[0042] An ana-ZMOF pure membrane was fabricated and fully characterized. The continuity of the membrane was tested by the separation of gas mixtures like CO₂/H₂ and CO₂/CH₄. Pursuant to these tests, ana-ZMOF showed a selectivity for CO₂ of 2.5 and 4, respectively. Figure 4 illustrates a scanning electron microscopy image with a view from the top of a zeolite-like metal-organic framework with ana topology membrane fabricated on alumina substrate. Figure 5 illustrates a scanning electron microscopy image with a view of the cross-section of a zeolite-like metal-organic framework with ana topology membrane fabricated on alumina substrate.

[0043] The use of ana-ZMOF to separate valuable highly branched paraffins from less valuable linear paraffins to enrich fuel is economically significant. Branched paraffins generally observe a higher octane rating than linear paraffins. This is particularly important in internal combustion engines, as high octane rating fuel results in less engine knocking and improved engine performance. On the other hand, diesel engines perform optimally with high cetane fuel because it readily ignites under pressures typically observed in a diesel engine. For diesel engines, linear paraffins are assigned a higher cetane rating number. Consequently, with respect to diesel fuel, linear paraffins are more valuable than branched paraffins. The ana-ZMOF’s ability to completely separate linear paraffins from branched paraffins, together with its high chemical stability, make it an ideal candidate as a kinetic-based adsorbent for fuel enrichment.
[0044] Figure 6 illustrates a representation of gasoline through a schematic view of isomers of hexane with their corresponding kinetic diameters and Research Octane Numbers (RON). Given the unique properties of ana-ZMOF, ana-ZMOF can kinetically separate n-hexane from its larger, higher RON isomers, such as 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane. Figure 7 illustrates a representation of the components of diesel fuel through a schematic view of paraffins with their corresponding kinetic diameters and Research Octane Numbers. Similarly, ana-ZMOF can kinetically separate n-hexane and n-octane from lower centane number paraffins with larger kinetic diameters, such as cyclohexane and 2,2,4-trimethylpentane. ana-ZMOF’s ability to separate other valuable paraffins will be readily apparent to one of skill in the art.
What Is Claimed Is:

1. A zeolite-like metal-organic framework composition, comprising:
   a metal-organic framework composition with ana topology characterized by the formula
   $[\text{M}^{III}(4, \text{5-imidazole dicarboxylic acid})_2\text{X(solvent)})_n$ wherein M$^{III}$ comprises a trivalent cation of
   a rare earth element, X comprises an alkali metal element or alkaline earth metal element, and
   solvent comprises a guest molecule occupying pores.

2. The composition of claim 1, wherein M$^{III}$ includes one or more of any one of the following
   trivalent cations of a rare earth element: Ce$^{3+}$, Dy$^{3+}$, Er$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Ho$^{3+}$, La$^{3+}$, Lu$^{3+}$, Nd$^{3+}$,
   Pr$^{3+}$, Pm$^{3+}$, Sm$^{3+}$, Sc$^{3+}$, Tb$^{3+}$, Tm$^{3+}$, Yb$^{3+}$, or Y$^{3+}$.

3. The composition of claim 1, wherein X includes one or more of lithium, sodium, potassium,
   rubidium, cesium, francium, beryllium, magnesium, calcium, strontium, barium, and radium.

4. The framework of claim 1, wherein the zeolite-like metal-organic framework with ana
   topology is anionic.

5. The composition of claim 1, wherein the pore sizes of the zeolite-like metal-organic
   framework with ana topology are tunable to within a range of less than about 0.5 Å.

6. The composition of claim 1, wherein the pore sizes of the zeolite-like metal-organic
   framework with ana topology are tuned to about 4.2 Å to 5.0 Å.

7. The composition of claim 1, wherein the zeolite-like metal-organic framework with ana
   topology is one or more of a thin film membrane and a zeolite molecular sieve.

8. The composition of claim 1, wherein the zeolite-like metal-organic framework with ana
   topology is an adsorbent for separating paraffins by size.

9. The composition of claim 8, wherein separating paraffins by size is kinetically driven.

10. The composition of claim 8, wherein separating paraffins by size includes separating
    isoparaffins from paraffins.
11. The framework of claim 8, wherein separating paraffins by size includes separating linear paraffins from branched paraffins.

12. The framework of claim 8, wherein n-pentane is kinetically separated from isopentane.

13. The framework of claim 8, wherein separating paraffins by size includes separating one or more of linear paraffins and mono-branched paraffins from 2,2,4-trimethylpentane.

14. A method of separating paraffins, comprising:

   contacting a zeolite-like metal-organic framework with ana topology with a flow of paraffins, and

   separating the paraffins by size.

15. The method of claim 14, wherein separating paraffins by size is kinetically driven.

16. The method of claim 14, wherein separating paraffins by size includes separating isoparaffins from paraffins.

17. The method of claim 14, wherein separating paraffins by size includes separating linear paraffins from branched paraffins.

18. The method of claim 14, wherein n-pentane is kinetically separated from isopentane.

19. The method of claim 14, wherein separating paraffins by size includes separating one or more of linear paraffins and mono-branched paraffins from 2,2,4-trimethylpentane.

20. The method of claim 14, wherein the zeolite-like metal-organic framework with ana topology is characterized by the formula $[M^{III}(4, 5\text{-}imidazole \text{ dicarboxylic acid})_2X(solvent)_a]_n$ wherein $M^{III}$ comprises a trivalent cation of a rare earth element, $X$ comprises an alkali metal element or alkaline earth metal element, and solvent comprises a guest molecule occupying pores.
21. The method of claim 20, wherein M\\textsuperscript{III} includes one or more of any one of the following trivalent cations of a rare earth element: Ce\\textsuperscript{3+}, Dy\\textsuperscript{3+}, Er\\textsuperscript{3+}, Eu\\textsuperscript{3+}, Gd\\textsuperscript{3+}, Ho\\textsuperscript{3+}, La\\textsuperscript{3+}, Lu\\textsuperscript{3+}, Nd\\textsuperscript{3+}, Pr\\textsuperscript{3+}, Pm\\textsuperscript{3+}, Sm\\textsuperscript{3+}, Sc\\textsuperscript{3+}, Tb\\textsuperscript{3+}, Tm\\textsuperscript{3+}, Yb\\textsuperscript{3+}, or Y\\textsuperscript{3+}.

22. The method of claim 20, wherein X includes one or more of lithium, sodium, potassium, rubidium, cesium, francium, beryllium, magnesium, calcium, strontium, barium, and radium.

23. The method of claim 14, wherein paraffins with high research octane numbers are separated from paraffins with low research octane numbers.

24. The method of claim 23, wherein the paraffins with low research octane numbers include one or more of linear paraffins and mono-branched paraffins.

25. The method of claim 14, wherein paraffins with high cetane numbers are separated from paraffins with low cetane numbers.

26. The method of claim 14, wherein paraffins with a kinetic diameter of greater than about 4.2Å to 5.0Å are separated from paraffins with a smaller kinetic diameter.
FIG 1
FIG 2

FIG 3
FIG 4

FIG 5
FIG 6

n-hexane (3.8-4.3 Å)

3-methylpentane (5 Å)

2,3-dimethylbutane (5.6 Å)

2,2-dimethylbutane (6.2 Å)

FIG 7

n-hexane (3.8-4.3 Å)

Cyclohexane (6 Å)

n-Octane (4.3 Å)

2,2,4-trimethylpentane (6.2 Å)
INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/056144

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G25/00 B01J20/22
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)
C10G B01J

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>AU 2015 201 045 B2 (EXXONMOBIL RES &amp; ENG CO) 13 August 2015 (2015-08-13) paragraphs [0080], [0088]; claims 1,3</td>
<td>1-13</td>
</tr>
</tbody>
</table>

[X] Further documents are listed in the continuation of Box C. [X] 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 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

** 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

* 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

++ 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
20 January 2017

Date of mailing of the international search report
06/02/2017

Name and mailing address of the ISA/
European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-0040,
Fax: (+31-70) 340-3016

Authorized officer:
Deurinck, Patricia

Form PCT/ISA2/210 (second sheet) (April 2005)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 2015/081237 A1 (UNIV KING ABDULLAH SCI &amp; TECH [SA]; EDDAOUDI MOHAMED [SA]) 4 June 2015 (2015-06-04) page 2, lines 11-15,22 - line 24; claims 1,20,27; example 1 page 4, line 7 - line 20 page 9, line 31 - page 10, line 3</td>
<td>1-26</td>
</tr>
<tr>
<td>X,P</td>
<td>WO 2016/048693 A1 (UNIV KING ABDULLAH SCI &amp; TECH [SA]; EDDAOUDI MOHAMED [SA]) 31 March 2016 (2016-03-31) L: priority date of present application document is not valid; page 17, lines 1-3, 18 - line 27; claims 2,3,6-9,20; example 2 page 1, line 29 - line 32 page 18, line 9 - line 27</td>
<td>1-26</td>
</tr>
</tbody>
</table>
**INTERNATIONAL SEARCH REPORT**

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

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

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-26

   a zeolite-like metal-organic framework composition, comprising a metal-organic framework composition with ana topology characterized by the formula \([\text{MIII (4, 5-imidazole dicarboxylic acid)}_2 \times (\text{solvent})_a \text{]}_n\) and a process using a zeolite-like metal-organic framework composition with ana-topology;

1.1. claims: 1-13

   a zeolite-like metal-organic framework composition, comprising a metal-organic framework composition with ana topology characterized by the formula \([\text{MIII (4, 5-imidazole dicarboxylic acid)}_2 \times (\text{solvent})_a \text{]}_n\)

1.2. claims: 14-26

   A method of separating paraffins, comprising contacting a zeolite-like metal-organic framework with ana topology with a flow of paraffins, and separating the paraffins by size.

---
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>AU 2015201045 B2</td>
<td>13-08-2015</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>US 2007202038 A1</td>
<td>30-08-2007</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 101432070 A</td>
<td>13-05-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1988996 A2</td>
<td>12-11-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2009528251 A</td>
<td>06-08-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 20090004891 A</td>
<td>12-01-2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2007202038 A1</td>
<td>30-08-2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2013023402 A1</td>
<td>24-01-2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2007101241 A2</td>
<td>07-09-2007</td>
</tr>
<tr>
<td>WO 2015081237 A1</td>
<td>04-06-2015</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 2014354691 A1</td>
<td>16-06-2016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2932066 A1</td>
<td>04-06-2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 105934267 A</td>
<td>07-09-2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 3074115 A1</td>
<td>05-10-2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 20166096630 A</td>
<td>16-08-2016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2016296883 A1</td>
<td>13-10-2016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2015081237 A1</td>
<td>04-06-2015</td>
</tr>
<tr>
<td>WO 2006116340 A1</td>
<td>02-11-2006</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 26093135 A1</td>
<td>02-11-2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1877412 A1</td>
<td>16-01-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2006287190 A1</td>
<td>21-12-2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2006116340 A1</td>
<td>02-11-2006</td>
</tr>
<tr>
<td>WO 2016048693 A1</td>
<td>31-03-2016</td>
<td>NONE</td>
<td></td>
</tr>
</tbody>
</table>