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(54) **Title:** A PROCESS FOR THE DEHYDROGENATION OF ALIPHATIC HYDROCARBONS

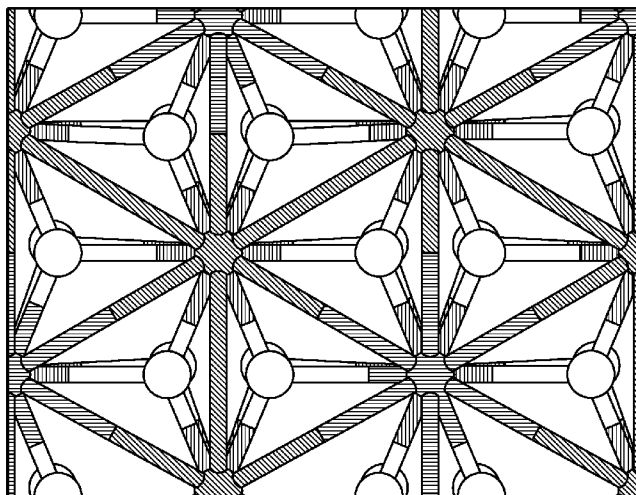


Fig. 5A

(57) **Abstract:** A process for the dehydrogenation of aliphatic hydrocarbons to form olefins, which involves selecting a dehydrogenation catalyst comprising Cr in the form of Cr_2O_3 and a heat transfer media on a Al_2O_3 catalyst support, and comprises an effective ratio of Cr to metal in the heat transfer media, passing an aliphatic hydrocarbon feed stream into a fixed-bed reactor comprising the selected dehydrogenation catalyst, and dehydrogenating the aliphatic hydrocarbon feed stream with the selected dehydrogenation catalyst. The Cr and the heat transfer media are evenly distributed on the Al_2O_3 catalyst support, and a higher yield is provided using a catalyst with the effective ratio of Cr to the heat transfer media than with a dehydrogenation catalyst containing only Cr_2O_3 on the Al_2O_3 catalyst support.



A PROCESS FOR THE DEHYDROGENATION OF ALIPHATIC HYDROCARBONS

BACKGROUND OF THE DISCLOSURE

TECHNICAL FIELD

[0001] The present disclosure relates to a process for the dehydrogenation of aliphatic hydrocarbons, whereby a dehydrogenation catalyst with a catalytic metal and a heat transfer media is selected using molecular modeling.

DESCRIPTION OF THE RELATED ART

[0002] The “background” description provided herein is for the purpose of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description which may not otherwise qualify as prior art at the time of filing, are neither expressly or impliedly admitted as prior art against the present disclosure.

[0003] Dehydrogenation reactions of hydrocarbon feedstock, such as the conversion of isobutane ($i\text{-C}_4\text{H}_{10}$) to isobutylene ($i\text{-C}_4\text{H}_8$), are widely implemented in the petrochemical industry. Dehydrogenation reactions are typically endothermic owing to the relatively high bond strength of C-H bonds and thus have a large activation energy for reactivity. For example, the dehydrogenation of isobutane to isobutene involves an input of 117.28 kJ per mole of energy at 298 K. As a result of the endothermic nature, a continuous heat supply is required to overcome the large activation energy for reactivity and to initiate the dehydrogenation reaction. Unfortunately, such high temperatures also affect the selectivity of the process as they tend to favor pyrolysis or cracking of the alkanes over dehydrogenation. One strategy to overcome the large activation energy for reactivity is the use of catalysts. Chromia-based catalysts are one of the most utilized catalysts for dehydrogenation reactions, and can significantly lower the reaction temperature requirements for reactivity.

[0004] One example of a catalytic dehydrogenation process is the CATOFINTM process. In the CATOFINTM process, the dehydrogenation of the hydrocarbon feedstock and the regeneration of the catalyst, or decoking, alternate in a cyclic or repetitive manner. Both dehydrogenation and regeneration are designed to run adiabatically, with the catalyst on the hydrocarbon feed for very short cycles, followed by regeneration of the catalyst for a similar period of time. Since the CATOFINTM process is designed to be adiabatic, and in order to prevent a decrease in alkane conversion, the consumption of heat during the endothermic

dehydrogenation process needs to be closely in balance with the heat restored to the bed during the exothermic regeneration cycles.

[0005] In conventional CATOFINTM processes, the reactor contains a physical mixture of a chromia/alumina catalyst and an α -alumina catalyst support. The catalyst support is used as a heat sink to supply heat during the dehydrogenation reaction. In a CATOFINTM process, the reactor or the catalyst bed is purged with hot air during the regeneration cycle in order to reheat the catalyst and remove coke which has been deposited on the catalyst bed during the endothermic dehydrogenation step. However, since the duration of the regeneration cycle is short, there is a strong likelihood for the formation of a vertical temperature gradient and pressure drop across the catalyst bed, which adversely affects the overall yield of the olefin product. Hence, with hot air flow and combustion of coke as the sole heat sources, heat input to the catalyst bed remains a critical limiting factor to CATOFINTM dehydrogenation processes.

[0006] More recently, an alternative approach towards heat transfer to the fixed CATOFINTM catalyst bed was developed using a material referred to as a “heat transfer media”. Heat transfer media is a catalyst additive material that, like the dehydrogenation catalyst, is also mounted on a catalyst support and meets several key performance parameters. In particular, heat transfer media produce heat in situ during the reducing and/or oxidizing conditions of a CATOFINTM regeneration cycle, and are inactive or inert to the hydrocarbon or alkane feed and the olefin products. Further, this media must not negatively impact the activity, selectivity or lifetime of the dehydrogenation catalyst (U.S. Patents 7,622,623 and 7,973,207; Oviol, L, Bruns, M, Fridman, V, Merriam, J, Urbancic, M, “Mind the gap”, published by Clariant Catalysis and Energy, formerly Süd-Chemie – each incorporated herein by reference in its entirety). Therefore, heat transfer media must provide heat storage (material with relatively high heat capacity), heat distribution (material with a high conductance) and heat addition to the catalyst bed without being directly involved in the dehydrogenation reaction.

[0007] New catalysts are often discovered using a trial-and-error method. This approach can often be expensive and time consuming, and significant effort is required to examine catalytic activity and selectivity using various types of reactors (i.e., micro, bench-scale, and pilot-scale reactors), reaction conditions, and characterization techniques. Prior to performing high-cost experimental synthesis and empirical reaction analysis, one alternative strategy is to apply a molecular modeling approach. Molecular modeling provides a high

throughput analysis technique, this enables a large number of catalysts to be analyzed in a quick and efficient manner, and allows for a facile analysis of the generated data set. Moreover, molecular modeling enables one to calculate properties of the catalysts that are extremely difficult or impossible to measure experimentally, such as catalyst adsorption energies.

[0008] In view of the forgoing, one aspect of the present disclosure is to provide a process for the dehydrogenation of aliphatic hydrocarbons whereby a dehydrogenation catalyst with an effective ratio of a catalytic metal and a heat transfer media is selected with molecular modeling.

BRIEF SUMMARY OF THE DISCLOSURE

[0009] The foregoing paragraphs have been provided by way of general introduction, and are not intended to limit the scope of the following claims. The described embodiments, together with further advantages, will be best understood by reference to the following detailed description taken in conjunction with the accompanying drawings.

[0010] In an embodiment, a process for the dehydrogenation of aliphatic hydrocarbons to form olefins, comprises: selecting a dehydrogenation catalyst based on its adsorption energy, wherein the dehydrogenation catalyst comprises Cr in the form of Cr_2O_3 and a heat transfer media on a Al_2O_3 catalyst support, and comprises an effective ratio of Cr to metal in the heat transfer media; passing an aliphatic hydrocarbon feed stream into a fixed-bed reactor comprising the selected dehydrogenation catalyst; and dehydrogenating the aliphatic hydrocarbon feed stream with the selected dehydrogenation catalyst; wherein the Cr and the heat transfer media are evenly distributed on the Al_2O_3 catalyst support.

[0011] The above described and other features are exemplified by the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Refer now to the drawing, which are exemplary and not limiting.

[0013] Fig. 1 is an illustration of bulk for $\alpha\text{-Al}_2\text{O}_3$.

[0014] Fig. 2A is an illustration of a side view of Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) with 18 layers and Fig. 2B is an illustration of a side view of O-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) with 18 layers.

[0015] Fig. 3A is an illustration of a side view of Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) and Fig. 3B is an illustration of a top view of Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001).

[0016] Fig. 4A is an illustration of a top view of absorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 1$) and Fig. 4B is an illustration a side view of absorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 1$).

[0017] Fig. 5A is an illustration of a top view of absorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 0.67$) and Fig. 5B is an illustration a side view of absorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 0.67$).

[0018] Fig. 6A is an illustration of a top view of absorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 0.33$) and Fig. 6B is an illustration a side view of absorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 0.33$).

[0019] Fig. 7A is an illustration of a top view of absorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 0.00$) and Fig. 7B is an illustration a side view of absorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 0.00$).

[0020] Fig. 8 is a graph of adsorption energies of adsorbed $\text{Cu}_x\text{Cr}_{1-x}$ on Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) ($x = 1.00, 0.67, 0.33, \text{ or } 0.00$). The more negative is the more stable.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0021] Referring now to the drawings.

[0022] According to a first aspect, the present invention relates to a process for the dehydrogenation of aliphatic hydrocarbons to form olefins comprising selecting a dehydrogenation catalyst comprising Cr and a heat transfer media on a Al_2O_3 catalyst support based on its adsorption energy and an effective ratio of Cr to the heat transfer media present in the catalyst.

[0023] In one embodiment, the Cr present in the dehydrogenation catalyst is in the form of chromia (Cr_2O_3).

[0024] In one embodiment, the dehydrogenation catalyst comprises 0.1-30 wt%, preferably 1-25 wt%, more preferably 2-20 wt% of the chromia relative to the total weight of the dehydrogenation catalyst.

[0025] In terms of the present invention, in addition to chromia, it is envisaged that the dehydrogenation catalyst may be adapted to incorporate other metals or metal oxide catalysts that may catalyze dehydrogenation chemistry. Examples of metals or metal oxides thereof include, but are not limited to, aluminum, magnesium, zirconium, titanium, vanadium, nickel, rhodium, rhenium, iron, silicon, molybdenum, thorium, manganese, cerium, silver, lead, cadmium, calcium, antimony, tin, bismuth, cobalt, tungsten, and zinc.

[0026] Further, it is envisaged that the dehydrogenation catalyst may be adapted to incorporate dehydrogenation catalysts, in lieu of the Cr, such as zeolites, acid treated metal oxides (e.g. acid treated alumina), or acid treated clays. Zeolites are microporous, aluminosilicate minerals. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite. Synthetic catalysts may include composites of silica and alumina or other metal oxides, including silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, silicavanadia, as well as ternary combinations such as silica-alumina-magnesia, silica-alumina-zirconia, and silica-magnesia-zirconia. Other bifunctional catalysts include, platinum and/or rhodium doped zeolites, and platinum-alumina. Acid treated natural clays which may be suitable for use as the catalyst in the invention include kaolins, sub-bentonites, montmorillonite, fullers earth, and halloysite.

[0027] The dehydrogenation catalyst also includes a heat transfer media. In terms of the present process, “heat releasing materials” or “heat transfer materials” or “heat transfer media” are materials that provide additional heat to an endothermic process as a result of the material undergoing a chemical reaction. The additional heat generated from the heat releasing material will then aid in driving the endothermic process towards completion. In regard to the present process, the heat transfer media is a material that is separate and additional to the Cr catalyst in a catalyst system designed for hydrocarbon dehydrogenation processes. Unlike the dehydrogenation catalyst, the heat transfer media is capable of producing heat in situ while remaining inactive or inert to the hydrocarbon or alkane feed and the olefin products. When oxidized or reduced, the heat transfer media will generate heat and conduct the heat into the dehydrogenation catalyst support, wherein the transferred heat may then be utilized during a subsequent dehydrogenation reaction. The characteristics and properties of one type of the heat transfer material are defined in U.S. Patent 7,622,623, which is incorporated herein by reference in its entirety.

[0028] Like the dehydrogenation catalyst, the heat transfer media of the present disclosure generally includes a metal and/or an oxide thereof. In one embodiment, the heat transfer media is copper. In one embodiment, the copper heat transfer material may be in a reduced state, i.e. elemental copper. Alternatively, the copper present in the dehydrogenation catalyst bed composition may be in a higher oxidation state (e.g. Cu^{+1} or Cu^{+2}). When in a higher oxidation state, the copper may be in an oxide form, for example CuO . Cu of the present process is selected as heat transfer media because it can easily oscillate between

higher and lower oxidation states and produce heat during both oxidation and reduction reactions, whereby the heat generated may be utilized in subsequent dehydrogenation reactions. It is envisaged that the present process may be adapted to incorporate other heat releasing media, in lieu of, or in addition to Cu. Other such heat releasing media may include, but is not limited to, silver, gold, aluminum, tungsten, platinum, etc.

[0029] The dehydrogenation catalyst can comprise 1 wt% to 20 wt%, for example, 1 wt% to 10 wt% or 5 wt% to 15 wt% of the heat transfer media relative to the total weight of the dehydrogenation catalyst.

[0030] For purposes of the present process the catalyst support refers to a high surface area material to which a catalyst is affixed. The support may be inert or may participate in catalytic reactions. In the present process, it is advantageous for the catalyst support to be inert to the dehydrogenation reaction. The reactivity of heterogeneous catalysts and nanomaterial-based catalysts occurs at the surface atoms. Consequently great effort is made to maximize the surface area of a catalyst by distributing it over the support. Typical supports include various kinds of carbon, alumina, and silica. In one embodiment, the catalyst support is aluminum oxide. The catalyst support may be comprised of a plurality of different crystallographic phases. Therefore, in terms of alumina, the catalyst support may comprise α -Al₂O₃, γ -Al₂O₃, η -Al₂O₃, θ -Al₂O₃, χ -Al₂O₃, κ -Al₂O₃, and δ -Al₂O₃, or a combination comprising at least one of the foregoing, for example, the catalyst support is γ -Al₂O₃, or the catalyst support is α -Al₂O₃.

[0031] In terms of the present process, an important characteristic of the catalyst support is its ability to store and distribute heat to aid in the catalytic process. One measure of the ability to distribute heat is the thermal conductivity. Heat transfer occurs at a higher rate across materials of high thermal conductivity than across materials of low thermal conductivity. During the dehydrogenation reaction, excess heat carried by the inert material should be dissipated along the catalyst bed. Therefore, a catalyst support with a high thermal conductance, such as Al₂O₃, is advantageous. One measure of the ability to store heat is the specific heat capacity. Heat capacity is a measurable physical quantity equal to the ratio of the heat added to (or subtracted from) an object to the resulting temperature change. Heat capacity is an extensive property of matter, meaning it is proportional to the size of the system. When expressing the same phenomenon as an intensive property, the heat capacity is divided by the amount of substance, mass, or volume, so that the quantity is independent of the size or extent of the sample. The specific heat capacity, therefore, is the heat capacity per

unit mass of a material. Temperature reflects the average randomized energy of constituent particles of matter (e.g. atoms or molecules), while heat is the transfer of thermal energy across a system boundary into the body or from the body to the environment. Translation, rotation, and a combination of the two types of energy in the vibration (kinetic and potential) of atoms represent the degrees of freedom of motion which classically contribute to the heat capacity of matter. On a microscopic scale, each system particle absorbs thermal energy among the few degrees of freedom available to it, and at sufficient temperatures, this process contributes to the specific heat capacity. Therefore, a catalyst support with a high specific heat capacity, such as Al_2O_3 , is advantageous.

[0032] In one embodiment, the catalyst support used in the molecular modeling was $\alpha\text{-Al}_2\text{O}_3$. The $\alpha\text{-Al}_2\text{O}_3$ can have a hexagonal crystal structure with a R-3C space group. The surface energies of a crystal lattice were calculated with terminal Al groups or terminated O groups of the $\alpha\text{-Al}_2\text{O}_3$. The surface energy was lower with terminal Al groups than with terminal O groups. Therefore, a crystal lattice with terminal Al groups is more stable than one with terminal O groups.

[0033] The molecular modeling can be performed with DFT calculations.

[0034] The surface energy of the $\alpha\text{-Al}_2\text{O}_3$ catalyst support with terminal Al groups can be 0.5 Joules per square meter (J/m^2) to 5 J/m^2 , preferably 1 J/m^2 to 4 J/m^2 , more preferably 2.5 J/m^2 to 3.5 J/m^2 . For example, the surface energy of the $\alpha\text{-Al}_2\text{O}_3$ catalyst support with terminal Al groups can be 2.95 J/m^2 .

[0035] The surface energy of the $\alpha\text{-Al}_2\text{O}_3$ catalyst support with terminal O groups can be 5 J/m^2 to 15 J/m^2 , preferably 8 J/m^2 to 12 J/m^2 , more preferably 10.5 J/m^2 to 11.5 J/m^2 . For example, the surface energy of the $\alpha\text{-Al}_2\text{O}_3$ catalyst support with terminal O groups can be 10.81 J/m^2 .

[0036] The selecting can be based on modeling the Al_2O_3 catalyst support with five active sites for supporting a metal, and the active sites comprise either oxygen or aluminum terminal groups. The five active sites that are suitable for supporting a metal using the most stable Al-terminated plane include three Al sites (Al1, Al3, and Al4) and two O sites (O2 and O5).

[0037] The preferential adsorption of the Cr and the Cu metals onto specific active sites was determined by calculating the adsorption energies of the metals onto each active site. Therefore, each metal can be placed into each active site, one by one, and the adsorption

energy can be calculated. In one embodiment, the Cr is preferentially adsorbed onto the two O sites. The Cr is preferentially adsorbed onto the O5 active site.

[0038] The Cr can be adsorbed on the oxygen terminating active site O5 with an adsorption energy of -1.7 electron volts (eV) to -1.5 eV, preferably -1.68 eV to -1.55 eV, more preferably -1.65 eV to -1.58 eV.

[0039] The Cu can be preferentially adsorbed onto the Al4 active site.

[0040] The heat transfer media, which is copper, can be adsorbed on the aluminum terminated active site Al4 with an adsorption energy of -0.95 eV to -0.75 eV, preferably -0.93 eV to -0.80 eV, more preferably -0.90 eV to -0.85 eV.

[0041] The selecting can be based on adsorption energy calculations for supporting Cr and the heat transfer media on the active sites of the Al_2O_3 . For example, the selecting can be based on adsorption energy calculations for supporting Cr on an oxygen terminating active site and the heat transfer media on the aluminum terminated active site of the Al_2O_3 .

[0042] Based on a preference to bind different sites to the Al_2O_3 catalyst support, a catalyst that contains a mix of Cr and Cu may be more stable than a catalyst with only one metal, wherein the sole metal would need to occupy all sites of the support, regardless of favorable or non-favorable adsorption energies.

[0043] The adsorption energy for a catalyst comprising only Cr supported on Al_2O_3 is -2.65 eV to -2.4 eV, preferably -2.6 eV to -2.45 eV, more preferably -2.55 eV to -2.5 eV. The adsorption energy for a catalyst comprising a ratio of Cr:Cu of 1:1 to 3:1 supported on Al_2O_3 is -2.8 eV to -2.6 eV, preferably -2.78 eV to -2.65 eV, more preferably -2.75 eV to -2.7 eV. The adsorption energy for a catalyst comprising only Cu supported on Al_2O_3 is -2.4 eV to -2.2 eV, preferably -2.37 eV to -2.25 eV, more preferably -2.35 eV to -2.3 eV. The adsorption energy for a catalyst comprising a ratio of Cr:Cu of 1:1 to 1:3 supported on Al_2O_3 is -2.75 eV to -2.55 eV, preferably -2.73 eV to -2.6 eV, more preferably -2.7 eV to -2.65 eV.

[0044] The effective ratio of Cr to metal in the heat transfer media can be 1:4 to 4:1. For example, the effective ratio of Cr to the metal (e.g., Cu) is 1:1 to 3:1. Wherein an effective ratio can be a ratio which provides a higher dehydrogenation yield than a dehydrogenation catalyst containing only Cr_2O_3 on an Al_2O_3 catalyst support (an amorphous gamma alumina support).

[0045] It is envisaged that the addition of a Cu heat releasing material may improve the yield of a dehydrogenation process by supplying additional heat. However, it is believed that too much copper present on the surface of the dehydrogenation catalyst may form a Cu

film. This copper film may prevent a hydrocarbon substrate from adsorbing onto the catalyst surface, and block access to the Cr catalytic metal. Therefore, for purposes of the present process, the ratio of Cu:Cr should not exceed 1:1.

[0046] The selected dehydrogenation catalyst with an effective ratio of Cr to the heat transfer media can be synthesized and used in a dehydrogenation process. The selected catalysts are synthesized by mixing together a Cr salt and a Cu salt. The Cr-Cu salt mixture may then be applied to the catalyst support. For example, and without limitation, the catalyst may be prepared by precipitation or impregnation of the Cr and Cu onto the catalyst support. Alternatively, the salt may be supported onto the Al_2O_3 support in sequential fashion, whereby the Cr salt is first supported, followed by supporting the Cu salt, or whereby the Cu salt is first supported, followed by supporting the Cr salt. Once the metals are both supported on the catalyst support, the supported mixture is then calcined to provide the oxides of both Cr and Cu. The Cr salt can be chromium nitrate. The Cu salt can be copper nitrate.

[0047] The ratio of Cr salt to Cu salt mixed together and/or supported on the Al_2O_3 catalyst can be 1:1 to 4:1, preferably 1.5:1 to 3.5:1, more preferably 1.7:1 to 3:1, even more preferably 1.8:1 to 2.5:1, even more preferably 1.9:1 to 2.1:1.

[0048] Once a dehydrogenation catalyst is selected and synthesized, the process next involves passing an aliphatic hydrocarbon feed stream into a fixed-bed reactor comprising the selected dehydrogenation catalyst.

[0049] The process then involves dehydrogenating the aliphatic hydrocarbon feed stream with the selected dehydrogenation catalyst.

[0050] Hydrocarbon dehydrogenation is the process whereby organic molecules, such as isobutane, are broken down to form corresponding alkenes, such as isobutene. During this process, the carbon-hydrogen bonds of the alkane are broken to form carbon-carbon double bonds. In addition to isobutane, other simple hydrocarbons such as ethane, propane, butane, etc., or C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , etc. may be dehydrogenation substrates. Hydrocarbon dehydrogenation reactions are typically endothermic reactions and have a high heat of reaction, and thus require high temperatures for reactions to occur. The heat of reaction, or enthalpy of reaction, is the change in the enthalpy of a chemical reaction that occurs at a constant pressure. Put another way, the heat of reaction is the amount of heat that must be added or removed during a chemical reaction in order to keep all of the substances present at the same temperature. Therefore, the use of heat transfer media is advantageous to supply extra heat to the dehydrogenation catalyst.

[0051] In terms of the present process, the chromia dehydrogenation catalyst, the Al_2O_3 catalyst support, and the heat transfer media are solid phase components that are mixed with each other to form the dehydrogenation catalyst. The catalyst support and the heat transfer media are catalytically inert in dehydrogenation processes. The Cr and the heat transfer media are evenly distributed on the Al_2O_3 catalyst support, and the effective ratio of Cr to the heat transfer media provides a higher dehydrogenation yield than a dehydrogenation catalyst containing only Cr on the Al_2O_3 catalyst support.

[0052] The reactors may be made of a silicon-oxygen framework (e.g. quartz) or a metal alloy (e.g. Inconel). The temperature of the continuous flow reactor can be, for example, controlled and maintained by a tube furnace.

[0053] In one embodiment, the dehydrogenation catalyst is homogeneously dispersed within the fixed-bed reactor. In terms of the present invention, the dehydrogenation catalyst is distributed throughout the fixed-bed reactor such that the properties of the dehydrogenation process (gas space velocity, yield, conversion, selectivity, etc.) meet the requirements of production.

[0054] In one embodiment, the process further comprises regenerating the selected dehydrogenation catalyst after dehydrogenating by passing an oxidizing gas over the catalyst bed then passing a reducing gas over the catalyst bed.

[0055] During regeneration, the air flows from the top of the catalyst bed to the bottom, and the regeneration cycle is relatively short, so there is a tendency for the top of the bed to be hotter than the bottom of the bed. The lower temperature in the bottom of the bed does not allow full utilization of the catalyst and thus the yield is lower than what would be otherwise expected. Also, the coke distribution in the catalyst bed, which is not easily controlled, affects the amount of heat added. This can lead to a non-uniform catalyst bed heating process and make the temperature profile in the bed difficult to control.

[0056] Passing an oxidizing gas over the selected dehydrogenation catalyst can oxidize the heat transfer media, and the oxidation of the heat transfer media generates additional heat that passes to the Cr and the catalyst support.

[0057] The oxidizing gas can be O_2 or air. Air may refer to natural air or synthetic air. For example, the oxidizing gas can be natural air. Natural air refers to the gaseous mixture that makes up the earth's atmosphere. Natural air comprises 77-79% N_2 , 20-21% O_2 , 0.9-1.0% Ar, and 0.03-0.04% CO_2 in terms of % volume. The oxidizing gas can be synthetic

air. Synthetic air is a gaseous mixture comprises 75-85% N₂ and 15-25% O₂ by volume. The oxidizing gas can be substantially pure O₂.

[0058] Passing a reducing gas over the selected dehydrogenation catalyst can reduce the heat transfer media, and the reduction of the heat transfer media generates additional heat that passes into the Cr and the catalyst support. A reducing gas may be any gas with a low oxidation number, and which is usually, but not always, hydrogen-rich. Examples of such reducing gasses include, but are not limited to, CH₄, H₂, NH₃, H₂S, and CO. The reducing gas can be CH₄ or H₂. The reducing gas can be a gaseous mixture comprising H₂ and an inert gas, wherein the H₂ is present in gaseous mixture in 1-95%, preferably 1-75%, more preferably 1-50%, even more preferably 1-40%, even more preferably 1-30%, even still more preferably 1-10% by volume relative to the total volume of the gaseous mixture. An inert gas refers to any gas that does not readily undergo chemical reactions. The inert gas source may be, but is not limited to, atomic nitrogen, helium, neon, argon, krypton, xenon, radon, and combinations comprising at least one of the foregoing. The inert gas can be Ar. The reducing gas can be pure H₂.

[0059] In one embodiment, the temperature effective for oxidizing the heat transfer media and the Cr catalyst is the same, which is 300-800°C, preferably 400-700°C, more preferably 500-600°C. In one embodiment, the temperature effective for reducing the heat transfer media and the Cr catalyst is the same, which is 300-800°C, preferably 400-700°C, more preferably 500-600°C.

[0060] During the reduction stage, the copper heat transfer material is reduced to a zero oxidation state (metallic state). Elemental copper behaves as an excellent conductive material, thus enhancing the heat conduction throughout the bed.

[0061] Lastly, the dehydrogenation process involves repeating the dehydrogenation process to form olefins.

[0062] The temperature of the selected dehydrogenation catalyst can be substantially uniform throughout the dehydrogenation process. Maintaining a uniform temperature gradient throughout the dehydrogenation catalyst of the fixed-bed reactor may help improve the dehydrogenation yield of the process.

[0063] The cyclic dehydrogenation process may additionally comprise a steam purge step after the dehydrogenation and prior to catalyst oxidation. Further, the cyclic process may also include an evacuation step in between the oxidation and reduction regeneration phase.

[0064] In one embodiment, the cyclic process also includes a reaction analyzer and a computer that are fluidly connected to the fixed-bed reactor, wherein the reaction analyzer detects changes in the reaction profile and the computer determines when the reaction is complete. The reaction analyzer may be, but is not limited to, a gas chromatogram, a mass spectrometer, an absorption spectrometer, a differential scanning calorimeter, or a combination thereof. Switching to the next step of the cyclic process described herein may also be automated by the computer. Therefore, the reaction analyzer and computer may be used in the present invention to identify and time complete dehydrogenation, oxidation and reduction of the dehydrogenation catalyst bed composition. For instance, the reaction analyzer and computer can detect when the dehydrogenation reaction is complete, and determine the proper time to switch to the catalyst regenerating sequence. Automating the gas switching process with a computer, may therefore impart even more accuracy into the cyclic process of the present invention, improving reaction yields and decreasing reaction cycle times.

[0065] It is envisaged that the process of the present invention may be utilized for reaction types other than hydrocarbon dehydrogenation reactions, where extra heat produced during the reaction is desired. By simply varying process parameters such as catalyst, catalyst support, reductive gas, or oxidative gas, the process of the present invention may be modified for alternative reactions such as hydrocarbon cracking reactions, coke production reactions, oxidation catalysts, or reduction catalysts.

[0066] The examples below are intended to further illustrate protocols for performing the dehydrogenation process.

EXAMPLE 1: Density functional theory (DFT) calculations

[0067] DFT calculations were carried out using the Vienna ab initio simulation package (VASP). The interaction between core and valence electrons was treated with the projector augmented wave (PAW) method, while the exchange-correlation interaction was described using the Perdew-Burke-Ernzerhof (PBE) functional. All calculations were carried out with a 415 eV kinetic energy cut-off for a plane wave basis set. Monkhorst-Pack meshes with $(3 \times 3 \times 3)$ and $(5 \times 5 \times 1)$ k-points were utilized for bulk and surface calculations, respectively. Adsorption energies (E_{ads}) were calculated by $E_{ads} = E(\text{adsorbate/alumina}) - E(\text{alumina}) - E(\text{adsorbate})$. $E(\text{adsorbate /alumina})$, $E(\text{alumina})$, and $E(\text{adsorbate})$ are the

calculated energies of an adsorbate on alumina, a bare alumina, and an adsorbate. To avoid interactions between slabs, a vacuum space of 15 Å was used.

EXAMPLE 2: Examination of the Validity of the Method

[0068] To prove the validity of the computational method used and before carrying out the calculation, the heat of reaction of reduction and oxidation were calculated as summarized in Table 1 which comprises the summary of experimental and computed results of Cu/CuO for oxidation and reduction at 0 K. The calculated results clearly show that the qualitative trend is in good agreement with the experiment, suggesting that the computational method would provide a reliable result. From the experiment and calculation, it was confirmed that the oxidation process is more exothermic than the reduction.

Table 1	
Cu + 1/2O ₂ → CuO at 0 K	
Experiment	−153.8 kJ/mol (−1.59 eV)
Prediction	−185.7 kJ/mol (−1.92 eV)
CuO + H ₂ → Cu + H ₂ O at 0 K	
Experiment	−85.1 kJ/mol (−0.88 eV)
Prediction	−132.4 kJ/mol (−1.37 eV)

[0069] In addition, the reduction and oxidation of Cr and Cr₂O₃ was simulated as summarized in Table 2 which comprises a summary of experimental and computed results of Cr/Cr₂O₃ for oxidation and reduction at 0 K. The computed result has the same trend as the experiment. Since the reduction of Cr₂O₃ is highly endothermic, its involvement in the redox process of Cu/CuO may be negligible. Therefore, the calculation supports that only the Cu/CuO pair is involved in the heat releasing process, while the Cr/Cr₂O₃ pair may be inert.

Table 2	
Cr + 3/4O ₂ → 1/2Cr ₂ O ₃ at 0 K	
Experiment	−564.4 kJ/mol (−5.85 eV)
Prediction	−580.4 kJ/mol (−6.02 eV)
Cr ₂ O ₃ + 3H ₂ → 2Cr + 3H ₂ O at 0 K	
Experiment	+412.1 kJ/mol (+4.27 eV)
Prediction	+206.5 kJ/mol (+2.14 eV)

EXAMPLE 3: Optimization of bulk α-Al₂O₃

[0070] Although amorphous gamma-alumina (γ-Al₂O₃) is used as a support, to simplify the calculation, alpha-alumina (α-Al₂O₃, Fig. 1) was used for the calculation, which

has a hexagonal structure of R-3C. The computed lattice parameters are in excellent agreement with experimental data as summarized in Table 3, which comprises the computed and experimental lattice parameter for α -Al₂O₃.

Table 3		
Lattice parameters	Computed	Experimental
a = b	4.7652	4.759
c	13.0079	12.991

EXAMPLE 4: Construction of the most stable surface (0001)

[0071] To carry out the surface calculations, the surface energies of Al- and O-terminated α -Al₂O₃ were examined. Among the low-index surfaces, α -Al₂O₃ (0001) is energetically the most stable. Thus in the surface calculations, only α -Al₂O₃ (0001) was applied. The surface energy calculations were performed using the equation in Table 4, which comprises a summary of surface energies of Al- and O-terminated α -Al₂O₃ (0001). The higher the surface energy, the more unstable. Therefore, as summarized in Table 4, the Al-terminated surface is more stable than the O-terminated surface. Fig. 2 displays that the side views of Al- and O-terminated α -Al₂O₃ (0001) with 18 layers.

[0072] To carry out surface calculations using the most stable Al-terminated plane, it is required to propose active sites. As summarized in Fig. 3, five active sites (Al1, Al3, Al4, O2, and O5) are available.

Table 4		
surface	surface energy (J/m ²)	remark
Al-terminated	2.95	Al-terminated surface is more stable.
O-terminated	10.81	
Surface energy = 1/(2S)·(E[surface] – E[bulk]). S = surface area		

[0073] As compiled in Table 5, the adsorption energies of Cu and Cr elements were predicted by placing them on the active sites one by one. It is demonstrated that Cu may be adsorbed at the Al4 site, while Cr may be occupied at the O5 site. Also, it demonstrated that Cr is more strongly adsorbed on the alumina support material than Cu (–1.64 eV versus –0.89 eV, respectively). Table 5 comprises a summary of adsorption energy (eV) of Cu or Cr on Al-terminated Al₂O₃ (0001).

Table 5				
active site	Cu	remark	Cr	remark
A11	+0.34		-0.25	
O2	-0.68		-1.59	
A13	-0.67		+1.60	
A14	-0.89	Most stable	-0.38	
O5	-0.70		-1.64	Most stable

[0074] Then, to understand the interaction of bimetallic $\text{Cu}_x\text{Cr}_{1-x}$ and the alumina support, the pure elements were changed to a mixture of Cu and Cr elements (see Fig. 4-7). As shown in Fig. 4-7, the distance of the Cr film from the surface is longer than that of the Cu film. Herein, the film means that the surface is fully covered with the Cr or Cu atoms. As a mixed metal catalyst with a Cr film and Cu atoms, the adsorption energies are increased. However, as Cu is more dominant, the adsorption energies become weaker. Fig. 8 clearly manifests that the $\text{Cu}_x\text{Cr}_{1-x}$ mixture is more strongly reacted with the support than a monometallic catalyst.

[0075] Because of the different preference of adsorption sites and the strength of Cr and Cu, Cr is energetically adsorbed on the support first and Cu would be adsorbed next. By using a mixture of Cr and Cu nitrates as precursors for Cr_2O_3 and CuO, after calcination, chromia may reside on the support first, and then, CuO in succession, for example, $\text{CuO/Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$. The topside of CuO may block the interaction of reactants (such as propane or isobutane) and the chromia catalysts, lowering the yield.

[0076] Set forth below are some embodiments of the process disclosed herein.

[0077] Embodiment 1: A process for the dehydrogenation of aliphatic hydrocarbons to form olefins, comprising: selecting a dehydrogenation catalyst based on its adsorption energy, wherein the dehydrogenation catalyst comprises Cr in the form of Cr_2O_3 and a heat transfer media on a Al_2O_3 catalyst support, and comprises an effective ratio of Cr to metal in the heat transfer media; passing an aliphatic hydrocarbon feed stream into a fixed-bed reactor comprising the selected dehydrogenation catalyst; and dehydrogenating the aliphatic hydrocarbon feed stream with the selected dehydrogenation catalyst; wherein the Cr and the heat transfer media are evenly distributed on the Al_2O_3 catalyst support; preferably the effective ratio of Cr to the heat transfer media provides a higher dehydrogenation yield than a dehydrogenation catalyst containing only Cr_2O_3 on the Al_2O_3 catalyst support.

[0078] Embodiment 2: The process of Embodiment 1, wherein the heat transfer media is copper oxide.

[0079] Embodiment 3: The process of any of the preceding Embodiments, wherein the selecting is based on modeling the Al_2O_3 catalyst support with five active sites for supporting a metal, and the active sites comprise either oxygen or aluminum terminal groups.

[0080] Embodiment 4: The process of any of the preceding Embodiments, wherein the selecting is based on adsorption energy calculations for supporting Cr and the heat transfer media on the active sites of the Al_2O_3 .

[0081] Embodiment 5: The process of any of the preceding Embodiments, wherein the selecting is based on adsorption energy calculations for supporting Cr on an oxygen terminating active site and the heat transfer media on the aluminum terminated active site of the Al_2O_3 .

[0082] Embodiment 6: The process any of the preceding Embodiments, wherein the Cr is adsorbed on an oxygen terminating active site with an adsorption energy of -1.7 to -1.5 eV.

[0083] Embodiment 7: The process of Embodiment 5, wherein the heat transfer media is adsorbed on an aluminum terminated active site with an adsorption energy of -0.95 to -0.75 eV.

[0084] Embodiment 8: The process of any of the preceding Embodiments, wherein the effective ratio of the Cr to the metal is 1:4 to 4:1.

[0085] Embodiment 9: The process of any of the preceding Embodiments, wherein the effective ratio of the Cr to the metal is 1:1 to 3:1.

[0086] Embodiment 10: The process of any of the preceding Embodiments, further comprising: regenerating the selected dehydrogenation catalyst after dehydrogenating by passing an oxidizing gas over the catalyst bed then passing a reducing gas over the catalyst bed, and repeating the dehydrogenation process to form olefins.

[0087] Embodiment 11: The process of Embodiment 10, wherein the oxidizing gas is O_2 or air.

[0088] Embodiment 12: The process of any of Embodiments 10 - 11, wherein the reducing gas is CH_4 or H_2 .

[0089] Embodiment 13: The process of any of Embodiments 10 - 12, wherein passing an oxidizing gas over the selected dehydrogenation catalyst oxidizes the heat transfer media, and the oxidation of the heat transfer media generates additional heat that passes to the Cr and the catalyst support.

[0090] Embodiment 14: The process of any of Embodiments 10 - 13, wherein passing a reducing gas over the selected dehydrogenation catalyst reduces the heat transfer media, and the reduction of the heat transfer media generates additional heat that passes into the Cr and the catalyst support.

[0091] Embodiment 15: The process of any of Embodiments 10 - 14, wherein the temperature of the selected dehydrogenation catalyst is substantially uniform throughout the dehydrogenation process; preferably the temperature of the selected dehydrogenation catalyst is 300-800°C; preferably the temperature of the selected dehydrogenation catalyst is 400-700°C; and more preferably the temperature of the selected dehydrogenation catalyst is 500-600°C.

[0092] Embodiment 16: The process of any of Embodiments 10 - 15, wherein the regenerating is at a temperature of 300-800°C; preferably 400-700°C; and more preferably 500-600°C.

[0093] Embodiment 17: The process of any of the preceding Embodiments, wherein the dehydrogenation catalyst has an adsorption energy of -2.8 eV to -2.6 eV, preferably -2.78 eV to -2.65 eV, more preferably -2.75 eV to -2.7 eV.

[0094] Embodiment 18: The process of any of Embodiments 1 - 17, wherein the dehydrogenation catalyst has an adsorption energy of -2.75 eV to -2.55 eV, preferably -2.73 eV to -2.6 eV, more preferably -2.7 eV to -2.65 eV.

[0095] Embodiment 19: The process of any of the preceding Embodiments, wherein the dehydrogenation catalyst comprises 1 wt% to 20 wt%, preferably, 1 wt% to 10 wt%, more preferably 5 wt% to 15 wt%, of the heat transfer media relative to the total weight of the dehydrogenation catalyst.

[0096] Embodiment 20: The process of any of the preceding Embodiments, wherein the dehydrogenation catalyst comprises 0.1-30 wt%, preferably 1-25 wt%, more preferably 2-20 wt% of Cr_2O_3 relative to the total weight of the dehydrogenation catalyst.

[0097] Embodiment 21: The process of any of the preceding Embodiments, wherein the Al_2O_3 comprises amorphous gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$).

[0098] Embodiment 22: The process of any of the preceding Embodiments, wherein the Al_2O_3 is amorphous gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$).

[0099] In general, the invention may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The invention may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components,

materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention.

[0100] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of “up to 25 wt%, or, more specifically, 5 wt% to 20 wt%”, is inclusive of the endpoints and all intermediate values of the ranges of “5 wt% to 25 wt%,” etc.). “Combination” is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms “first,” “second,” and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms “a” and “an” and “the” herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Reference throughout the specification to “one embodiment”, “another embodiment”, “an embodiment”, and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments. The present application claims priority to US Provisional Application No. 62/156,707, filed May 4, 2016, which is incorporated herein in its entirety.

[0101] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

CLAIMS

1. A process for the dehydrogenation of aliphatic hydrocarbons to form olefins, comprising:

selecting a dehydrogenation catalyst based on its adsorption energy, wherein the dehydrogenation catalyst comprises Cr in the form of Cr_2O_3 and a heat transfer media on a Al_2O_3 catalyst support, and comprises an effective ratio of Cr to metal in the heat transfer media;

passing an aliphatic hydrocarbon feed stream into a fixed-bed reactor comprising the selected dehydrogenation catalyst; and

dehydrogenating the aliphatic hydrocarbon feed stream with the selected dehydrogenation catalyst;

wherein the Cr and the heat transfer media are evenly distributed on the Al_2O_3 catalyst support, and the effective ratio of Cr to the heat transfer media provides a higher dehydrogenation yield than a dehydrogenation catalyst containing only Cr_2O_3 on the Al_2O_3 catalyst support.

2. The process of Claim 1, wherein the heat transfer media is copper oxide.

3. The process of any of the preceding claims, wherein the selecting is based on modeling the Al_2O_3 catalyst support with five active sites for supporting a metal, and the active sites comprise either oxygen or aluminum terminal groups.

4. The process of any of the preceding claims, wherein the selecting is based on adsorption energy calculations for supporting Cr and the heat transfer media on the active sites of the Al_2O_3 .

5. The process of any of the preceding claims, wherein the selecting is based on adsorption energy calculations for supporting Cr on an oxygen terminating active site and the heat transfer media on the aluminum terminated active site of the Al_2O_3 .

6. The process of any of the preceding claims, wherein the Cr is adsorbed on an oxygen terminating active site with an adsorption energy of -1.7 to -1.5 eV.

7. The process of any of the preceding claims, wherein the heat transfer media is adsorbed on an aluminum terminated active site with an adsorption energy of -0.95 to -0.75 eV.
8. The process of any of the preceding claims, wherein the effective ratio of Cr to the metal is 1:4 to 4:1.
9. The process of any of the preceding claims, wherein the effective ratio of Cr to the metal is 1:1 to 3:1.
10. The process of any of the preceding claims, further comprising regenerating the selected dehydrogenation catalyst after dehydrogenating by passing an oxidizing gas over the catalyst bed then passing a reducing gas over the catalyst bed, and repeating the dehydrogenation process to form olefins.
11. The process of Claim 10, wherein the oxidizing gas is O₂ or air.
12. The process of any of Claims 10 - 11, wherein the reducing gas is CH₄ or H₂.
13. The process of any of Claims 10 - 12, wherein passing an oxidizing gas over the selected dehydrogenation catalyst oxidizes the heat transfer media, and the oxidation of the heat transfer media generates additional heat that passes to the Cr and the catalyst support.
14. The process of any of Claims 10 - 13, wherein passing a reducing gas over the selected dehydrogenation catalyst reduces the heat transfer media, and the reduction of the heat transfer media generates additional heat that passes into the Cr and the catalyst support.
15. The process of any of Claims 10 - 14, wherein the temperature of the selected dehydrogenation catalyst is substantially uniform throughout the dehydrogenation process.

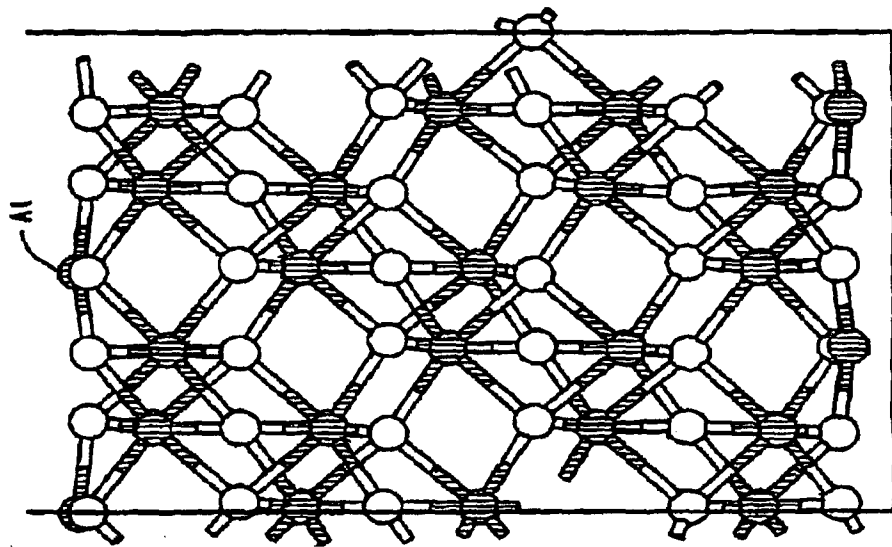


Fig. 2A

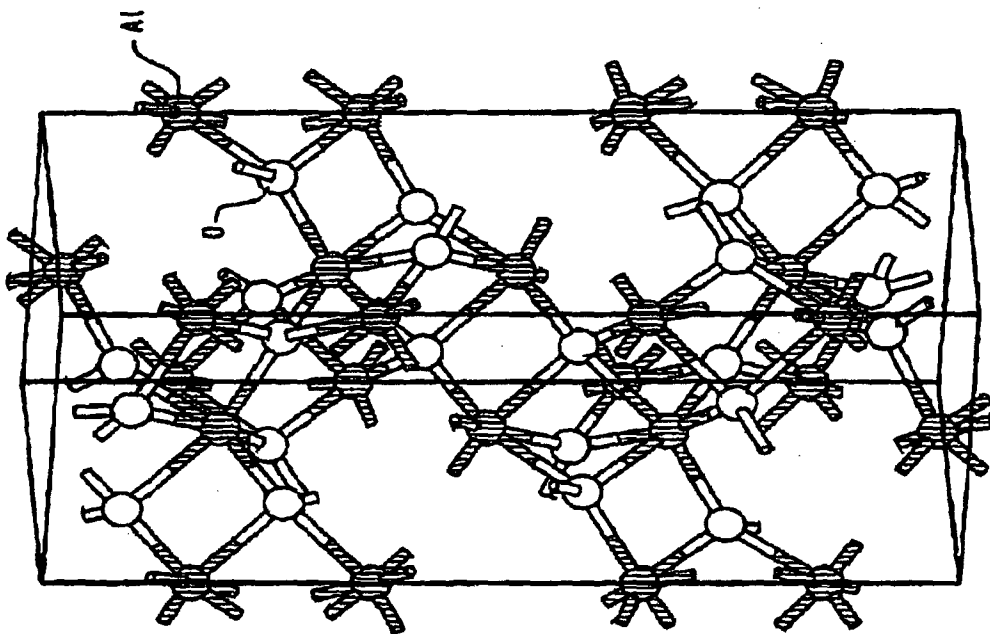
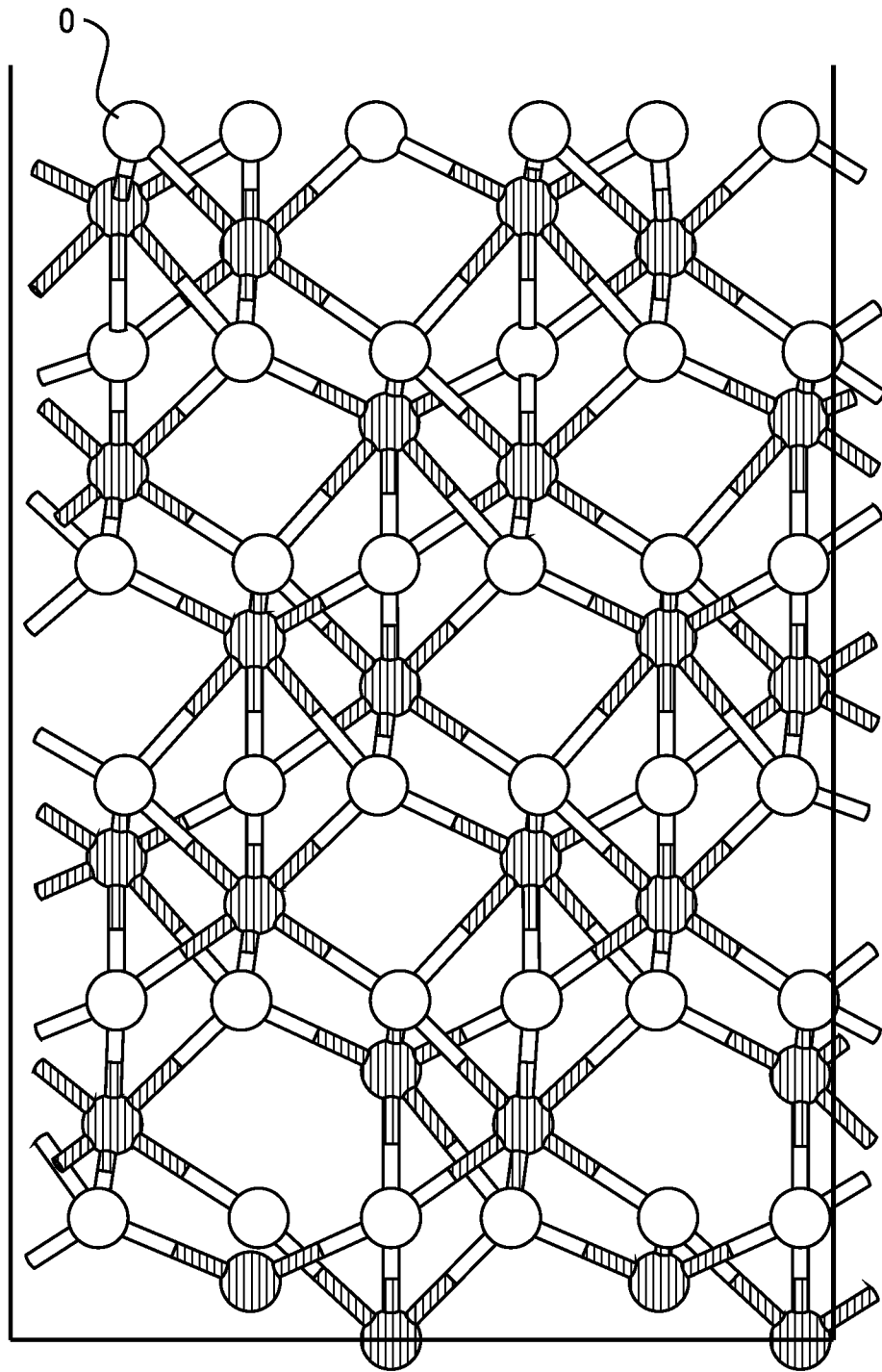


Fig. 1

*Fig. 2B*

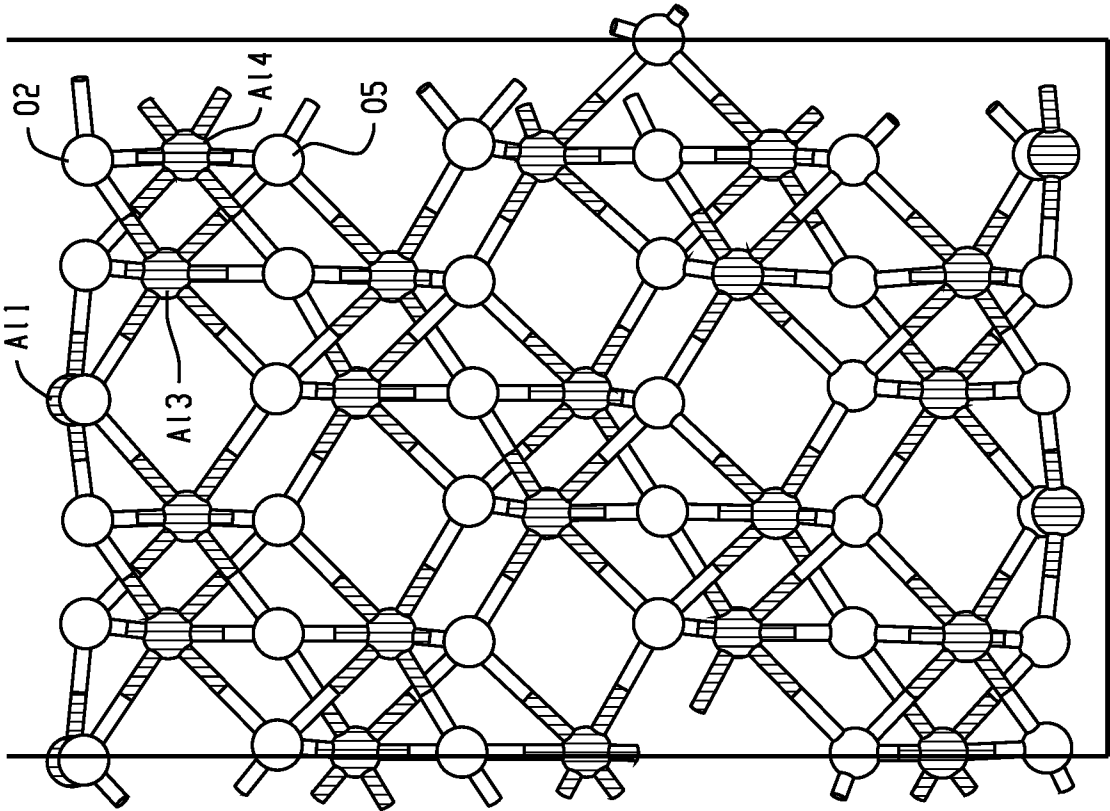


Fig. 3A

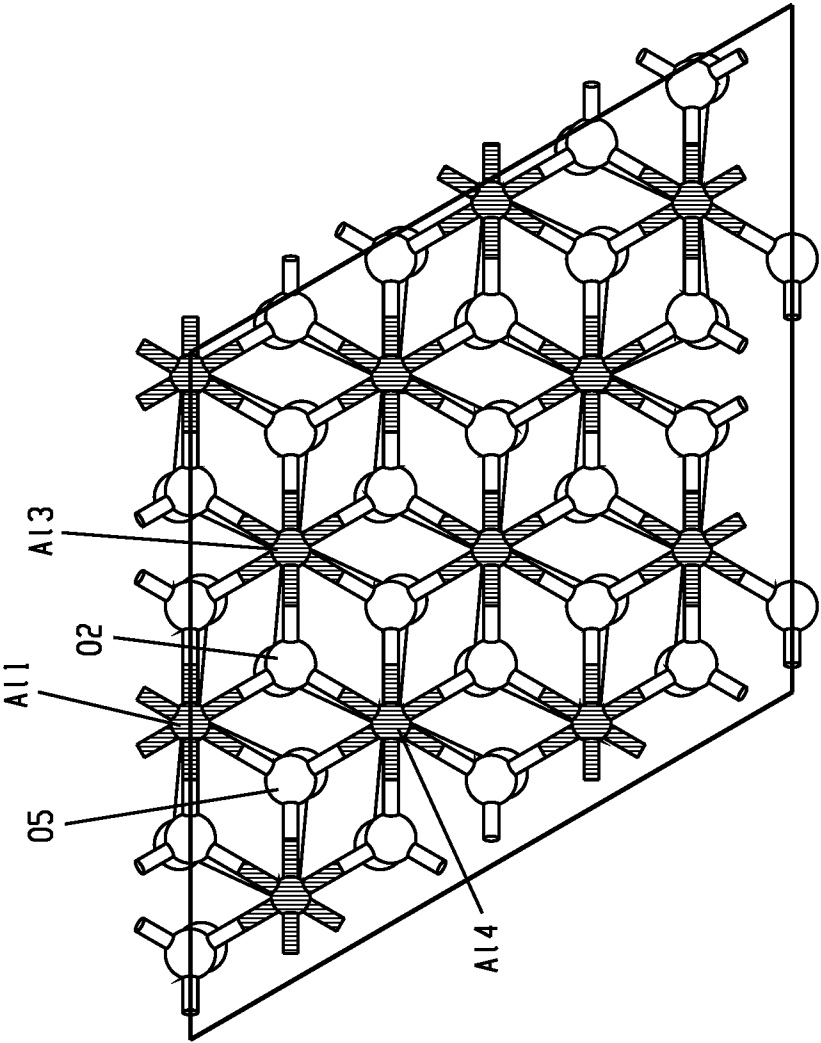
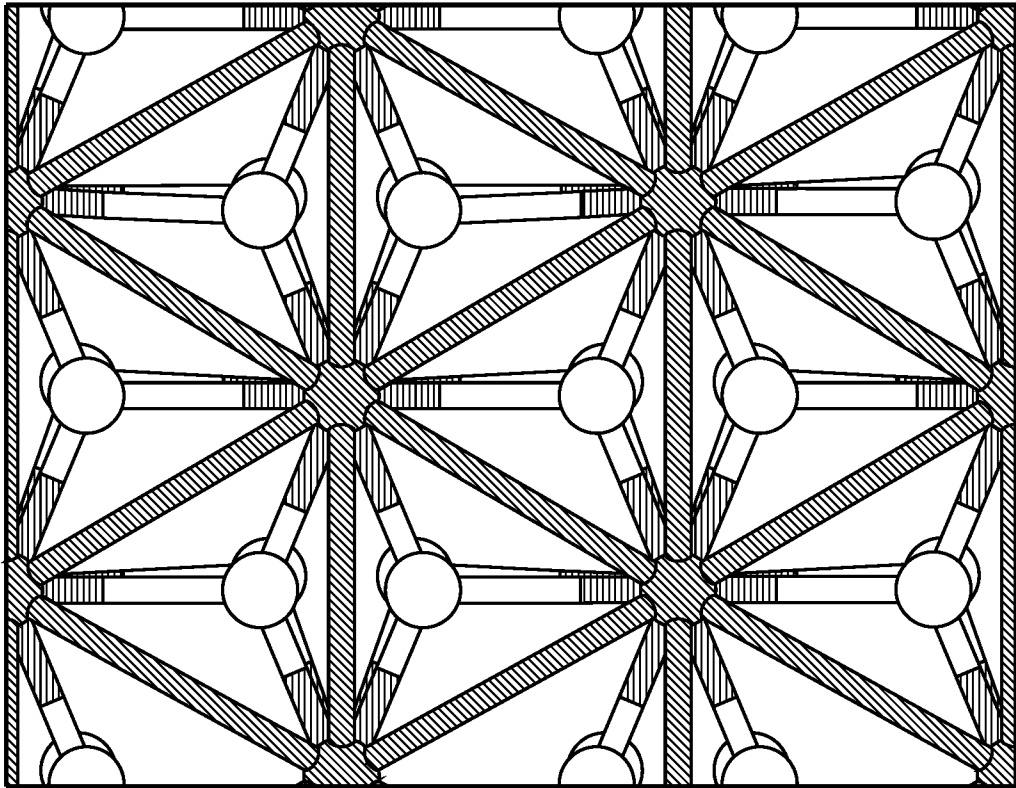
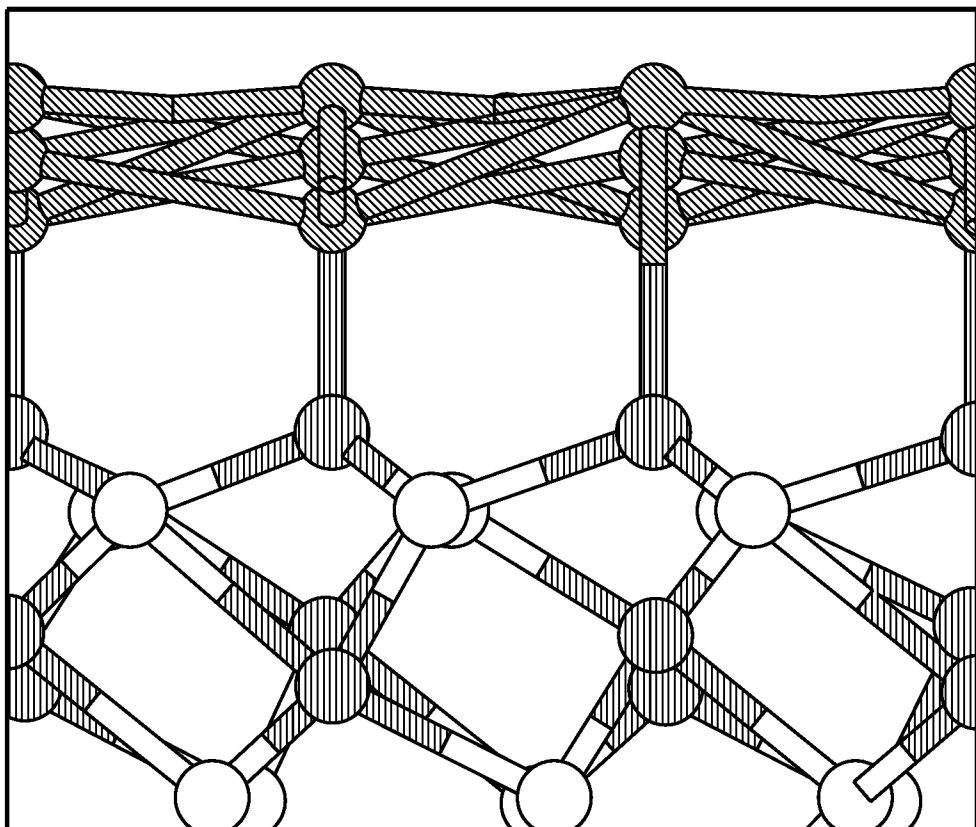
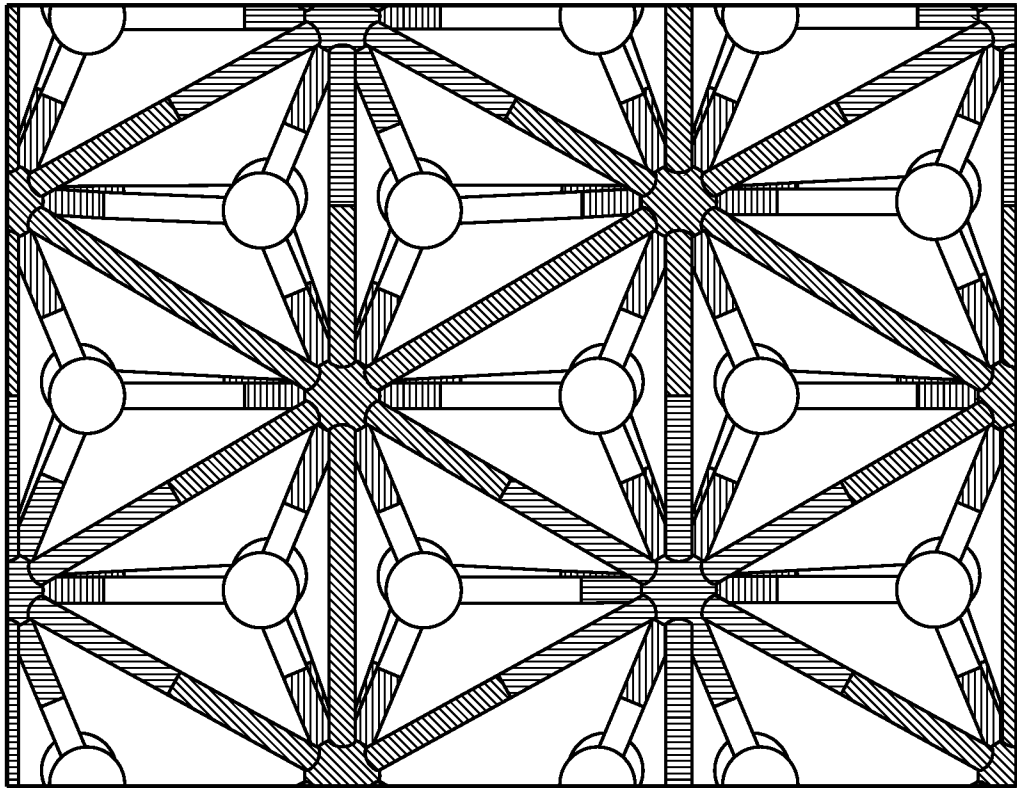
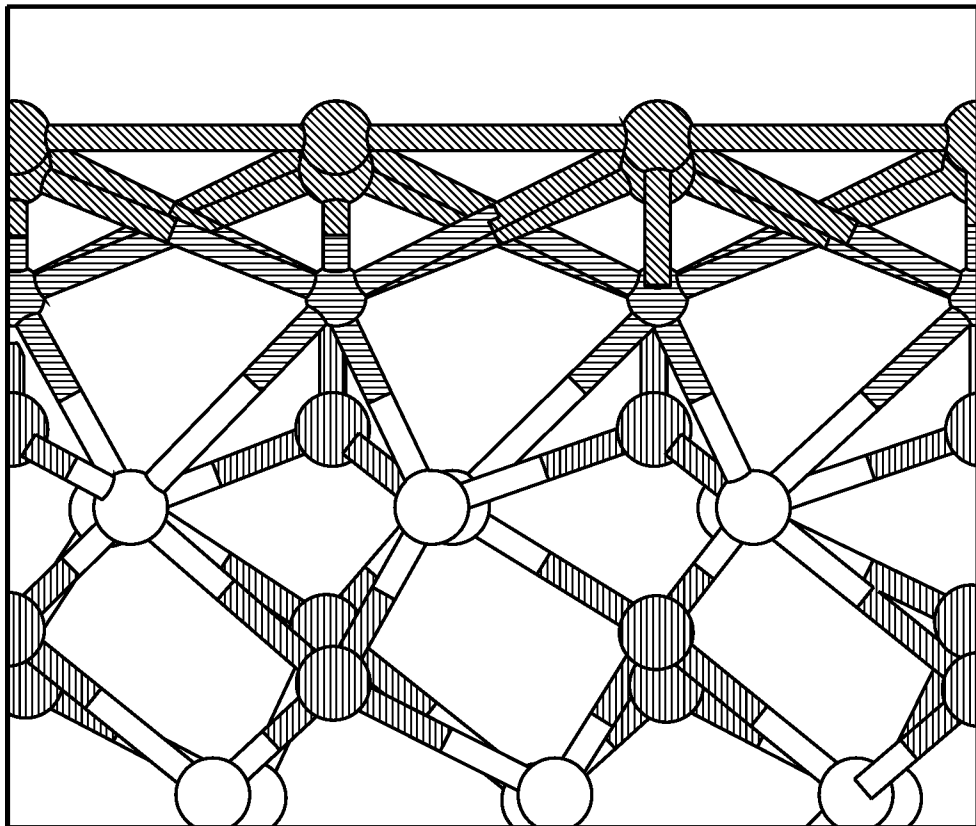
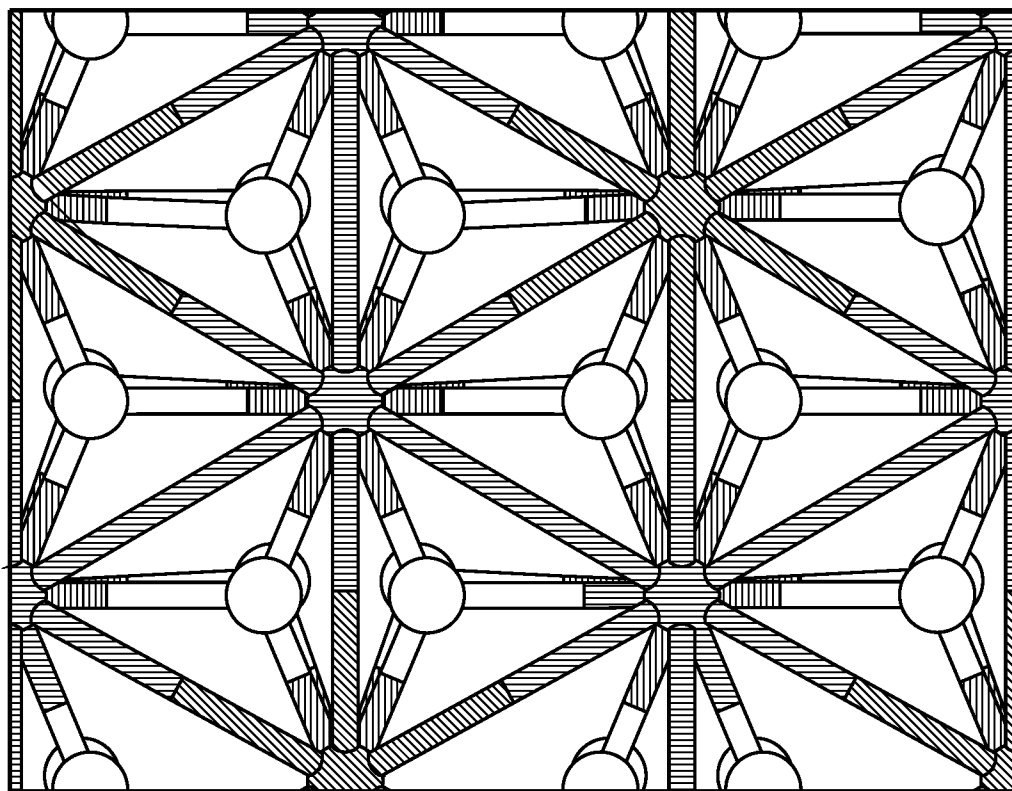
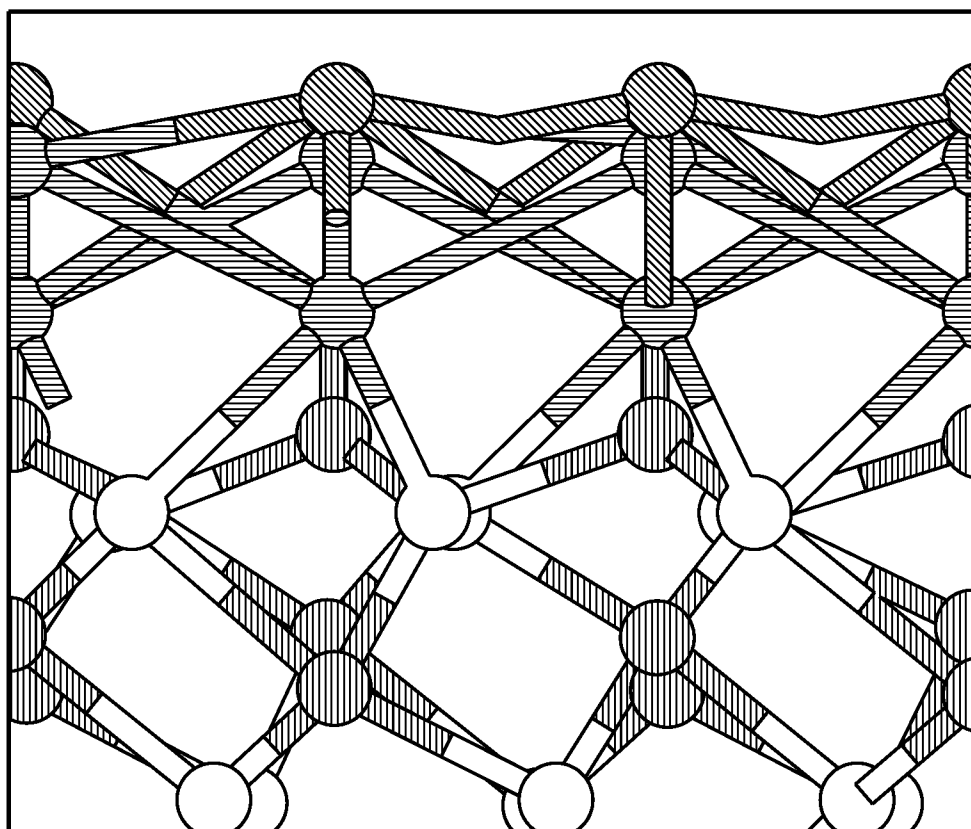


Fig. 3B

*Fig. 4A**Fig. 4B*

*Fig. 5A**Fig. 5B*

*Fig. 6A**Fig. 6B*

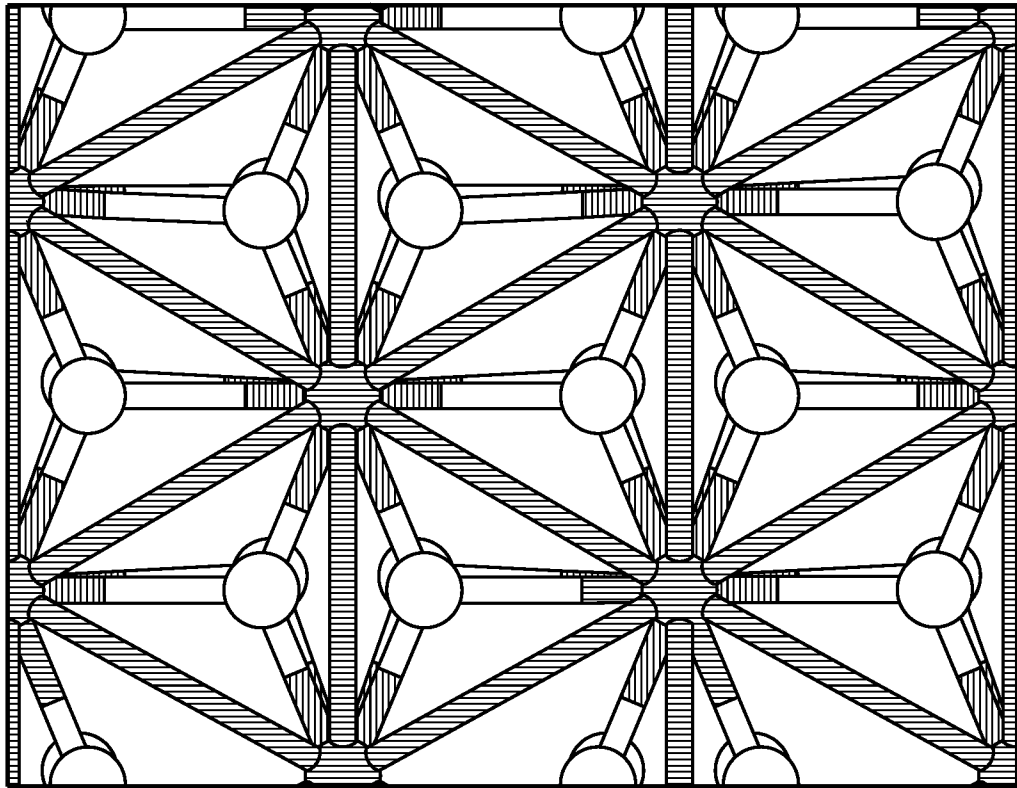


Fig. 7A

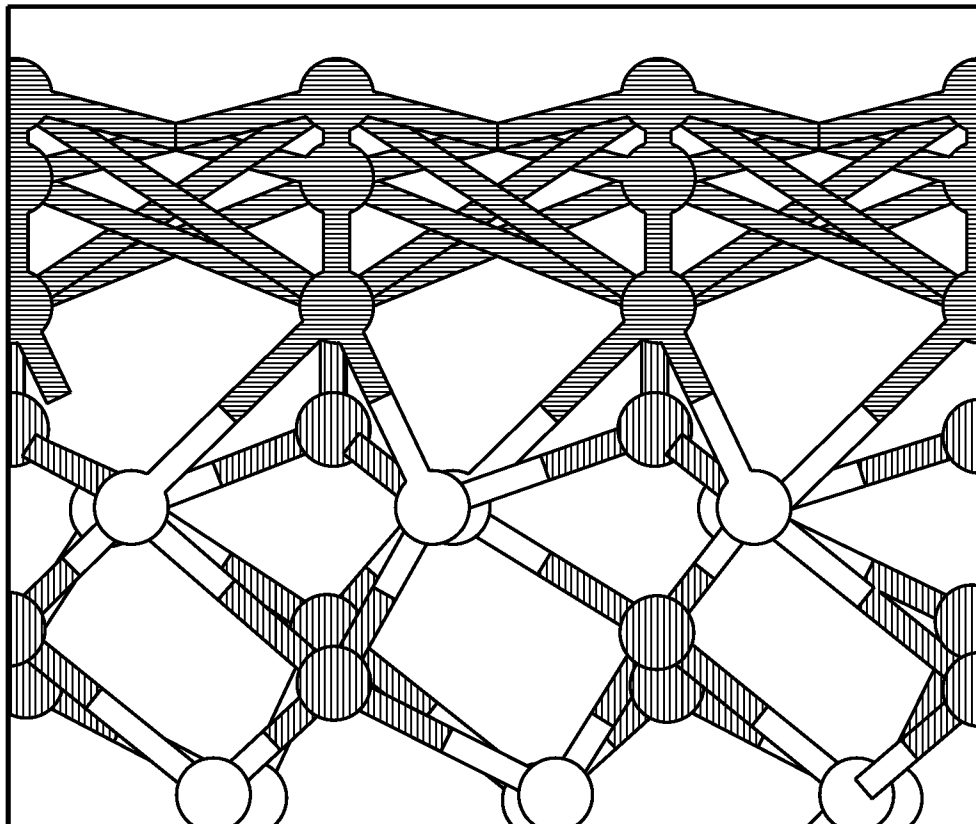


Fig. 7B

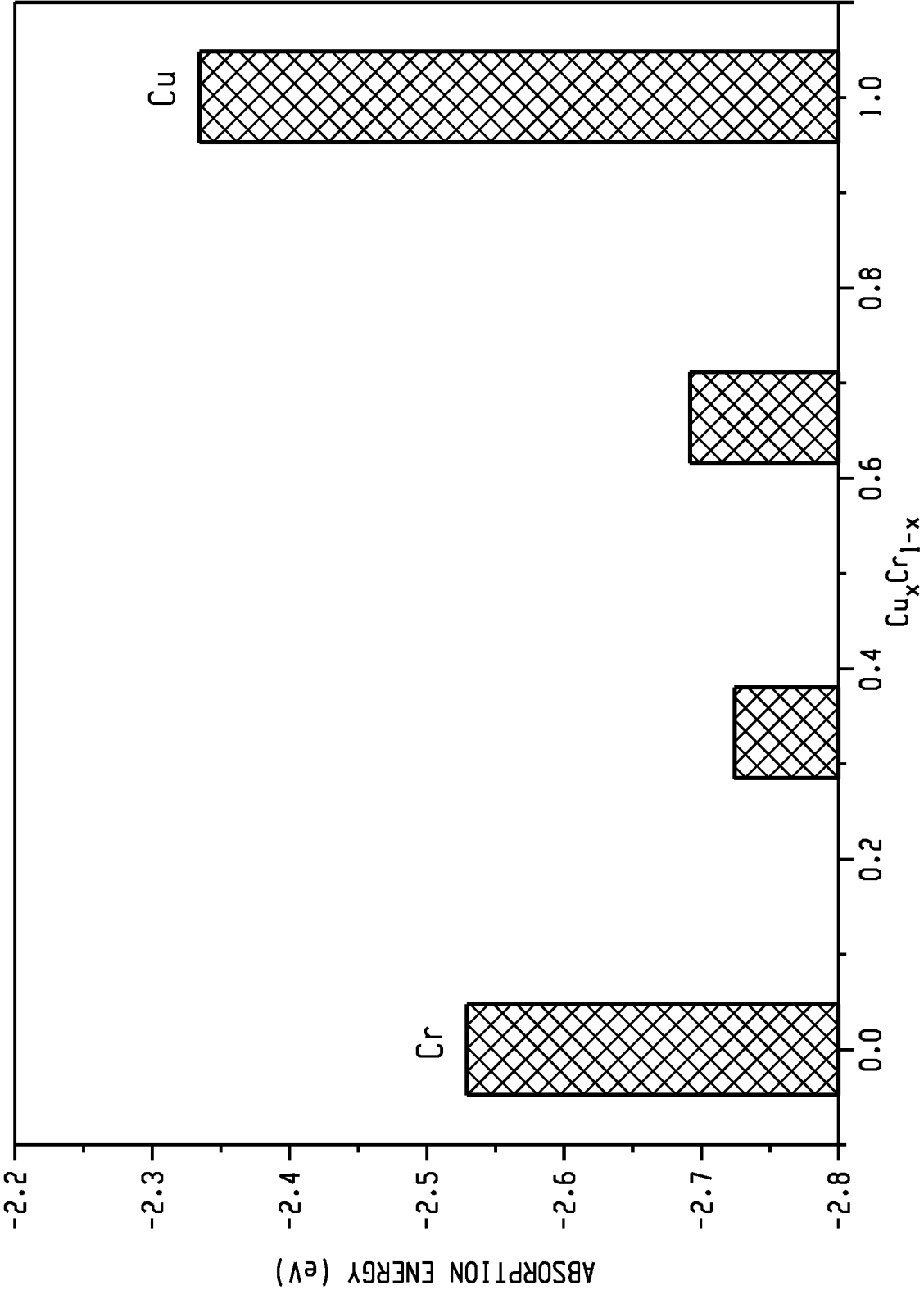


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/052482

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C5/333 B01J23/26
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)
C07C 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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/051767 A1 (SUED CHEMIE INC [US]; URBANCIC MICHAEL A [US]; FRIDMAN VLADIMIR [US]) 23 April 2009 (2009-04-23) example 5	1-15
A	----- WO 2007/030298 A1 (SUED CHEMIE INC [US]; FRIDMAN VLADIMIR [US]; MERRIAM JAY S [US]; URBAN) 15 March 2007 (2007-03-15) cited in the application the whole document -----	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

25 July 2016

Date of mailing of the international search report

01/08/2016

Name and mailing address of the ISA/

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Fritz, Martin

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2016/052482

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