(12) STANDARD PATENT (11) Application No. AU 2004268935 B2
(19) AUSTRALIAN PATENT OFFICE

(54) Title
Hydrocarbon synthesis

(51) International Patent Classification(s)
C07C 1/26 (2006.01)

(21) Application No: **2004268935** (22) Date of Filing: **2004.07.15**

(87) WIPO No: **WO05/021468**

(30) Priority Data

(31) Number	(32) Date	(33) Country
60/487,364	**2003.07.15**	**US**

(43) Publication Date: **2005.03.10**
(44) Accepted Journal Date: **2010.12.02**

(71) Applicant(s)
GRT, Inc.

(72) Inventor(s)
Stucky, Galen D.;Lorkovic, Ivan M.;Sherman, Jeffrey H.;Weiss, Michael J.;Noy, Maria

(74) Agent / Attorney
FB Rice & Co, Level 23 44 Market Street, Sydney, NSW, 2000

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 March 2005 (10.03.2005)

PCT

(10) International Publication Number
WO 2005/021468 A1

(51) International Patent Classification[7]: C07C 1/26

(21) International Application Number: PCT/US2004/023036

(22) International Filing Date: 15 July 2004 (15.07.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/487,364 15 July 2003 (15.07.2003) US

(71) Applicant (*for all designated States except US*): **GRT, INC.** [US/US]; 301 B South Wimbrow Drive, Sebastian, FL 32958 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **LORKOVIC, Ivan, M.** [US/US]; Santa Barbara, CA (US). **NOY, Maria** [US/US]; Santa Barbara, CA (US). **SHERMAN, Jeffrey, H.** [US/US]; 301 B South Wimbrow Drive, Sebastian, FL 32958 (US). **WEISS, Michael, J.** [US/US]; Santa Barbara, CA (US). **STUCKY, Galen, D.** [US/US]; Santa Barbara, CA (US).

(74) Agent: **CARPENTER, John, D.**; Christie, Parker & Hale, P.O. Box 7068, Pasadena, CA 91109-7068 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/021468 A1

(54) Title: HYDROCARBON SYNTHESIS

(57) Abstract: A method of synthesizing hydrocarbons from smaller hydrocarbons includes the steps of hydrocarbon halogenation, simultaneous oligornerization and hydrogen halide neutralization, and product recovery, with a metal-oxygen cataloreactant used to facilitate carbon-carbon coupling. Treatment with air or oxygen liberates halogen and regenerates the cataloreactant.

HYDROCARBON SYNTHESIS

FIELD OF THE INVENTION

This invention relates generally to hydrocarbon oligomerization, and more particularly to a method of making hydrocarbons using cataloreactants.

BACKGROUND OF THE INVENTION

Scientists have long sought efficient ways to convert methane and other alkanes into higher hydrocarbons, including light olefins and gasoline-range materials. Efficient processes could create value in a number of ways, including: facilitating the utilization of remotely located stranded natural gas through its conversion into more easily transportable liquid fuels and feedstocks, and allowing the use of inexpensive feedstocks (methane and other lower alkanes) for end products often made from higher alkanes, including ethylene and propylene.

U.S. Patent Nos. 6,486,368, 6,472,572, 6,465,699, 6,465,696, and 6,462,243 disclose processes for converting alkanes into olefins, ethers, and alcohols. Many of the disclosed processes involve halogenation of an alkane, passing the halogenated products over a metal oxide to create products and metal halide, recovering the product(s), and regenerating the metal halide with oxygen or air to yield metal oxide and halogen for recycle to the process. Not described is alkane oligomerization: substantial coupling of the starting hydrocarbon to obtain product(s) of higher carbon number.

Several investigators have examined the use of halogenation for the production of higher hydrocarbons from methane. Representative patents include 4,513,092 (Chu), 4,769,504 (Noceti and Taylor), 5,087,786 (Nubel), and 6,452,058 (Schweitzer). As described in the Taylor patent: "Aromatic-rich, gasoline boiling range hydrocarbons [are made] from the lower alkanes, particularly from methane. The process is carried out in two stages. In the first, alkane is reacted with oxygen and hydrogen chloride over an oxyhydrochlorination catalyst such as copper chloride with minor proportions of potassium chloride and rare earth chloride. This produces an intermediate gaseous mixture containing water and chlorinated alkanes. The chlorinated alkanes are contacted with a crystalline aluminosilicate catalyst in the hydrogen or metal-promoted form to produce gasoline range hydrocarbons with a high proportion of aromatics and a small percentage of light hydrocarbons (C_2–C_4), as well as reforming the HCl. The light hydrocarbons can be recycled for further processing over the oxyhydrochlorination catalyst." All of these techniques for making higher alkanes from C_1 feedstocks suffer from the disadvantage that the hydrocarbon stream must be separated from an aqueous hydrohalic acid stream, and the hydrohalic acid stream must be recycled.

US 4,795,843 (Tomotsu et al.) discloses a process for oligomerizing halomethanes to products including ethyl benzene, toluene, and xylenes, using silica polymorph or silicalite catalysts. The process does not incorporate reactive neutralization of hydrogen halide, and appears to suffer from slow kinetics.

In a process for halogenating hydrocarbons, Chang and Perkins noted trace amounts of oligomerization products in the presence of zeolites in US 4,654,449. The oligomerization products were low in quantity, and generally halogenated.

US 4,373,109 (Olah) discloses a process for converting heterosubstituted methanes, including methyl halides, by contacting such methanes with bifunctional acid-base catalysts at elevated temperatures, between 200 and 450 C, preferably between 250 and 375 C, to produce predominantly lower olefins, preferably ethylene and propylene. The catalysts of preference are those derived from halides, oxyhalides, oxides, sulfides or oxysulfides of transition metals of Groups IV, V, VI, VIII of the Periodic Table, such as tantalum, niobium, zirconium, tungsten, titanium, and chromium, deposited on acidic oxides and sulfides such as alumina, silica, zirconia or silica-alumina. Neither the use of solid oxide-based halogen recovery nor the formation of alcohols or ethers is disclosed. A related reference is "Ylide chemistry. 1. Bifunctional acid-base-catalyzed conversion of heterosubstituted methanes into ethylene and derived hydrocarbons. The onium-ylide mechanism of the C1→C2 conversion" by George A. Olah et al. (J. Am. Chem. Soc. 106, 2143 (1984)).

US 3,894,107 (Butter, et al.) discloses improvements to a process for condensing halogenated hydrocarbons using zeolite catalysts. Notably absent is any discussion of solid oxide-based hydrogen halide neutralization.

Kochi has observed reductive coupling of alkyl halides when transition metal bromides are reacted with low-molecular weight Grignard reagents in THF or diethyl ether (Bulletin of the Chemical Society of Japan v. 44 1971 pp.3063-73). Liquid phase chemistry, however, typically suffers from such disadvantages as the requirement of solvent, corrosion, and lower rates of reaction than gas-phase chemistry. In addition, such a process consumes energy required to produce the magnesium metal needed for the energetic and reducing Grignard reagents. This is not the same type of process as the dehydrohalogenative coupling and hydrogen halide neutralization we describe herein.

SUMMARY OF THE INVENTION

The present invention addresses the need for an efficient way to convert methane and other hydrocarbons into higher hydrocarbons. In one embodiment, a hydrocarbon having a carbon number C_n, where $n \geq 2$, is prepared by allowing a reactant hydrocarbon having a carbon number C_m, where $m < n$, to react with a halogenating agent, thereby forming a halogenated hydrocarbon; allowing the halogenated hydrocarbon to contact a metal-oxygen cataloreactant, thereby forming a product hydrocarbon having an carbon number C_n, where $n \geq 2$; recovering the product hydrocarbon; and regenerating the metal-oxygen cataloreactant. Often, a mixture of hydrocarbons is obtained, but careful selection of the reactant hydrocarbon, halogenating agent, metal-oxygen cataloreactant, and reaction conditions allow a tailored approach to hydrocarbon product formation. Methane (i.e., natural gas) as well as other light hydrocarbons, e. g., C_2 to C_6 hydrocarbons, are envisioned as preferred feedstocks.

Although laboratory observations have thus far focused on methane oligomerization with detection of ethylene, propylene, butenes and aromatics, the invention contemplates the use of feedstocks having carbon numbers as high as C_{10}.

DETAILED DESCRIPTION OF THE INVENTION

Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The present invention exploits the discovery that metal-oxygen compounds, such as mixed metal oxides, particularly metal oxide-impregnated zeolites, facilitate hydrocarbon oligomerization. According to one aspect of the invention, a hydrocarbon having a carbon number C_n, where $n \geq 2$, is formed by (i) forming a halogenated hydrocarbon by allowing a reactant hydrocarbon having a carbon number C_m, where $m < n$, to react with a halogenating agent; (ii) forming a product hydrocarbon having a carbon number C_n, where $n \geq 2$, by allowing the halogenated hydrocarbon to contact a metal-oxygen cataloreactant; (iii) recovering the product hydrocarbon; and (iv) regenerating the cataloreactant.

More generally, the method entails the steps of halogenation, oligomerization, product recovery, and cataloreactant regeneration. The halogenated products may be separated from the unreacted (non-halogenated) hydrocarbon either before or after reaction with the metaloxygen cataloreactant. Neutralization of any hydrohalic acid formed during the synthesis is advantageously accomplished concommitantly with carbon-carbon coupling and/or cataloreactant regeneration. Preferably, the process is an integrated one and takes place, for example, in a zone reactor, as described, for example, in U.S. 6,525,230 (Grosso), the entire contents of which is incorporated by reference herein. Thus, halogenation of methane or other hydrocarbons occurs within one zone of the reactor, and is followed by a condensation step in which the liberated hydrohalic acid is adsorbed within the same bifunctional material that catalyzes condensation of the halogenated hydrocarbon. Hydrocarbon oligomerization (defined as carbon-carbon coupling) takes place within this zone of the reactor and yields product hydrocarbons which, in general, will have carbon numbers ranging from C_2 to C_{20}, and may include alkanes, alkenes, alkynes, and/or aromatics. Treatment with air or oxygen liberates halogen for use in subsequent halogenation steps, and regenerates the cataloreactant material for subsequent condensation or metathesis. Advantageously, the need for recycling/recovering corrosive, aqueous hydrohalic acid is avoided because regeneration and recovery takes place in situ.

Higher hydrocarbon synthesis begins with a hydrocarbon feedstock: one or more reactant hydrocarbons, each having, independently, a carbon number C_m, where $m < n$, C_n being the carbon number of the target hydrocarbon(s). Non-limiting examples of reactant hydrocarbons include methane, ethane, propane, etc., with natural gas (predominately methane, but often including small amounts of C_2 and higher species) being preferred. In general, the starting hydrocarbon has a carbon number between 1 and 10. Mixtures of hydrocarbons may also be used.

The reactant hydrocarbons are allowed to react with a halogenating agent. Non-limiting examples include molecular halogen (e.g., bromine, chlorine, etc.), alkyl halides (e.g., dibromomethane, bromoform,carbon tetrabromide), and condensed halides, such as metal bromides, which may be present as a solid, liquid, supported, or unsupported material.

Molecular halogens are preferred, with bromine (Br_2) being most preferred. Bromine is a liquid at room temperature, less reactive than chlorine and fluorine, and easy to handle. Bromine also has favorable energetics.

The reduction potential of bromine to bromide is 1.07 V vs. NHE, while that of oxygen to water is 1.23 V. A broad range of metal bromides may release bromine upon treatment with oxygen. At the same time, alkane bromination and subsequent alkyl bromide coupling and HBr neutralization are only mildly exothermic, but spontaneous enough to go to completion. Water and coupled hydrocarbons are the only fluid products. The same is not true with chlorine as mediator, for which HCl is a major component of the product stream. Hydrogen chloride production requires separation, drying, and recycling, which is costly. In short, the thermochemistry of metal bromide-mediated alkane partial oxidiation is well-suited for efficient and inexpensive plant operation.

Halogenation of the reactant hydrocarbon may proceed in a number of ways, depending in part on the desired product(s) and in part on the feed. In one embodiment, an alkane is halogenated with molecular halogen using heat, light, or other electromagnetic radiation to drive the reaction, with heat being preferred. There is some benefit in having all steps -- halogenation, oligomerization, and regeneration (described below)-- occur at roughly the same temperature. As typical temperatures for methanol to olefin (MTO) and methanol to gasoline (MTG) processes, temperatures of from 375 to 450°C are utilized, with the range being important, if not critical. For the carbon-carbon coupling process described herein, an ideal temperature range, where all steps occur at roughly the same temperature, is 450 to 550°C. Alternatively, individual reaction steps might be carried out at temperatures above or below this range.

Halogenation preferably occurs at a pressure between 0.1 and 200 atm, for the subsequent carbon-carbon step. Low pressure favors less carbon-carbon coupling (i.e., a smaller average molecular weight of product), while high pressure favors higher coupling. Processes for light olefins are likely to run at the same 60 to 200 psia that methanol to olefin (MTO) processes are run at, although higher pressures may alternatively be utilized. For production of gasoline-range molecules, pressures around 350 psia, as used in methanol to gasoline (MTG) processes, are envisioned. As a practical matter, running below atmospheric (more conservatively, below 2 psia) or above 100 atm is unlikely.

When molecular halogen is used as the halogenating agent, halogenation ideally is carried out at an alkane:halogen ratio of between 1:10 and about 100:1, on a volume by volume basis. At alkane:halogen ratios of less than 1:10 (i.e., more halogen), multi-halogenated hydrocarbons will be formed, typically leading to complete oxidation (i.e., CO_2) upon subsequent contact with the metal-oxygen cataloreactant. At alkane:halogen ratios higher than 100:1, the conversion to a halogenated hydrocarbon will be too low, perhaps 1% or less, and it is nearly impossible to imagine an economical process at such conversion levels. (30-60% conversion are more likely lower limits).

Altering the ratio of halogen to alkane or other hydrocarbon feedstock may have a marked impact on product distribution. For example, one may choose to control the degree of halogenation in order to reduce aromatic formation in the production of lower olefins or fuels. A second example is minimizing formation of highly halogenated methane in order to reduce the formation of alkynes.

A key feature of the invention is the use of a metal-oxygen cataloreactant, which facilitates carbon-carbon coupling, i.e., hydrocarbon oligomerization. The term "metal-oxygen cataloreactant" is used herein to refer to a cataloreactant material containing both metal and oxygen. While not bound by theory, it is believed that the material catalyzes carbon-carbon coupling via hydrogen halide (e.g., HBr) elimination and alkylidene insertion into cationically activated C-H and possibly C-C bonds. The cataloreactant also acts as a halogen release and sequestering agent, and offers the possibility of obtaining a tunable coupling product distribution, including the ability to produce oxygenates if desired, while simultaneously trapping and recovering halogen, emitting only water as a byproduct. Treatment with air or oxygen regenerates the cataloreactant.

Nonlimiting examples of metal-oxygen cataloreactants include zeolites, doped zeolites, metal oxides, mixed metal oxides, metal oxide-impregnated zeolites, and similar materials, as well as mixtures of such materials. Nonlimiting examples of dopants include calcium and magnesium, and their oxides and/or hydroxides.

Zeolites are available from a variety of sources, including Zeolyst International (Valley Forge, PA). Specific examples include doped-ZSM-5 and doped mordenite (where, e.g., calcium and/or magnesium are the dopants).

Shifting the properties of the zeolite or zeolite component of a zeolite/metal oxide composite is also expected to shift product distribution. Pore size and acidity are particularly expected to be important. Acidity may be used to control chain length and functionality, and pore size may control chain length and functionality. Zeolites of particular pore-size may selectively produce benzene, toluene, para-xylene, ortho-xylene, meta-xylene, mixed xylenes, ethyl benzene, styrene, linear alkyl benzene, or other aromatic products. The use of pore size is not limited to aromatic products.

In one embodiment of the invention, a metal oxide/zeolite composite is prepared by mixing a zeolite with a metal nitrate (e.g., calcium nitrate) or hydrated species thereof.

After oligomerization, the metal-oxygen cataloreactant is regenerated by treatment with air or oxygen, typically at a temperature of from 200 to 900 °C. This converts metal halide species into metal-oxygen species.

A number of variables, including feed composition, feed location in the reactor, temperature, pressure, metal oxide composition, and reactor residence time may alter the product distribution. Production of alkanes, olefins and aromatics from methane has been detected and confirmed. Also expected is the ability to produce alkanes and olefins of particular branching (including mono-methyl branched alcohols), alcohols, diols, ethers, halogenated hydrocarbons, aromatics including benzene, styrene, ethyl benzene, toluene, xylenes, and linear alkyl benzenes, and hydrocarbons suitable for fuels such as gasoline, diesel, and jet fuel.

Control of the feed composition can control the product distribution. First, hydrogen halide produced in the halogenation may be neutralized (to form water or alcohol) with the same metal-oxygen compound producing the hydrocarbon product(s), or with a separate metal-oxygen compound in a distinct reactor. Shifting the hydrogen halide neutralization location may shift the product distribution, including functionality, chain length, and branching. For example, concurrent neutralization and product formation may be expected to drive the production of alcohols, which may or may not undergo further reactions such as coupling or dehydration. Second, water addition to the feed may shift product distribution. In particular, the addition of water may favor alcohol products. The addition of water may also control degree and type of branching and chain length. Third, hydrogen addition may alter the product distribution. Hydrogen may increase alkanes at the expense of other functionalities, something particularly useful for producing fuels. Hydrogen may also reduce coking and help control the chain length and branching.

It will also be appreciated that carbon-carbon oligomerization may proceed by a number of pathways. Even single-hydrocarbon feedstocks may yield more than one product. On the other hand, in one embodiment of the invention, controlled halogentation is used to produce predominately one isomer in favor of another (e.g., selective formation of 1-butene or 2-butene). Mixed feedstocks, such as raw natural gas, may give rise to oligomerization of multiple halogenated hydrocarbons (e.g., ethyl halide, dihaloethane, methyl halide, methyl dihalide, propyl halide, propyl dihalide, etc.). Indeed, in one embodiment of the invention, an alkyl halide is purposefully introduced to create desired branched products. An example would be oligomerization of methyl halide (from methane) with ethyl halide or a higher alkyl halide to produce, selectively, methyl, ethyl, propyl, isopropyl, or tertiary butyl (or other) branching. Another example might be the synthesis of styrene from ethyl halide, methyl halide, and dihalomethane.

In one embodiment of the invention, the reaction of halogenated hydrocarbon with a metal-oxygen cataloreactant takes place in a fluidized bed. Alternatively, a fixed bed is employed. Different alkyl halides may be introduced at different locations in the reactor. One example is the introduction of methyl halides at one location in a reactor to produce benzene, to which ethyl halides are added, producing styrene or ethyl benzene. Another example is the introduction of methyl halides at one location in a reactor to produce benzene, to which alkyl halides are added, producing linear alkyl benzene.

Product separation is accomplished by any suitable method. Nonlimiting examples include distillation, adsorption, and extraction. Product(s) may be recovered from the solid by stripping with steam, carbon dioxide, or other means.

The following are nonlimiting examples of the invention:

Example 1. Metal Oxide/Zeolite composite MZ1 was prepared as follows: A solid mixture of a ZSM-5-type zeolite (Zeolyst CBV 8014, Si/Al ratio = 80, 10 g, 170 mmoles SiO_2) and $CaNO_3$ nonahydrate (9 g, = 34 mmoles Ca) was prepared and water was added to incipient wetness. After $CaNO_3$ dissolution and stirring, the slurry was dried and calcined in sequence at 115 C (overnight) and 500 C (overnight), respectively, in air.

Example 2. Methane at 15 psia was bubbled through bromine at 1 °C at a rate of 5 cc/min. The resulting stream of bromine and methane (1:10 by mole) was passed through a small diameter bromination reactor at 450° C (1000 h^{-1}) and the mixture of $CH_{4-x}Br_x$ (x = 0, 1, 2, 3) passed into a reactor containing 5 g of metal oxide/zeolite composite MZ1 (400 C). The output stream from the second reactor contained no brominated products. Based on the methane consumed in the bromination reactor, 10% ethylene, 31% propylene, 3% propane, and 21% butanes/butenes were detected; 65% overall. Trace amounts of C_6 species were also detected. After reaction for 5 hours, during which the stream output did not change from the distribution described above, the methane stream was discontinued and the reactor was purged with helium at 5 cc/min for 10 minutes. After He purge, a flow of O_2 (2 cc/min) into the second reactor was initiated at 525 C to regenerate the metal oxide from the metal bromide of the partially spent composite. Initially only water and CO_2 were observed as products, but abruptly the stream contents changed to Br_2 and unreacted O_2. After 1 hour, the O_2 purge was discontinued and the reactor was again purged with helium. The caustic trap used during regeneration was tested for CO_3^{-2} and 1.0 mmol was found, representing 24% of the converted carbon. The remainder of carbon was found to be higher boiling volatile aromatics (mostly toluene, xylenes and mesitylenes). A second cycle of bromomethanes condensation as described above was initiated at 400°C and the product distribution was found to be identical to the first run. Three more cycles of condensation/ neutralization/ regeneration produced the same output of higher hydrocarbons.

Example 3. A doped mordenite (Zeolyst CBV 21A, doped with both Ca and Mg) (5g) was prepared according to Example 1, and used as the cataloreactant in a hydrocarbon synthesis substantially similar to that described above in Example 2. The product output was 30% ethylene, 5% ethane, 10% propylene, 3% propane, 5% butanes/butenes. Multiple runs and cataloreactant regeneration established reproducibility.

The invention has been described by reference to various examples and preferred embodiments, but is not limited thereto. Other modifications and substitutions can be made without departing from the scope of the invention. For example, the oligomerization processes described herein are also intended to encompass halogenation of olefin feedstocks using a hydrogen halide (e.g., HBr) or molecular halogen; halogenation of acetylenes (alkynes) using hydrogen halide or molecular halogen; halogenation of alcohols or ethers using hydrogen halide or molecular halogen; and halogenation of alkanes using molecular halogen and a catalyst that controls the halogenation. Specifically, the catalyst may control one or both of the degree of halogenation (number of halogens per molecule) and the position of halogenation (e.g. terminal vs. internal halogenation for a long chain alkane). Other modifications may be made as well. The invention is limited only by the appended claims and equivalents thereof.

2004268935 05 Nov 2010

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of making a hydrocarbon having a carbon number Cn, where n ≥ 2, comprising:

forming a halogenated hydrocarbon by allowing a reactant hydrocarbon having a carbon number C_m, where m < n, to react with a halogenating agent;

forming a product hydrocarbon having a carbon number C_n, where n ≥ 2, by allowing the halogenated hydrocarbon to contact a metal-oxygen cataloreactant;

recovering the product hydrocarbon; and

regenerating the cataloreactant.

2. A method as recited in claim 1, wherein the reactant hydrocarbon comprises methane.

3. A method as recited in claim 1, wherein the metal-oxygen cataloreactant is selected from the group consisting of zeolites, doped zeolites, metal oxides, mixed metal oxides, metal oxide-impregnated zeolites, and mixtures thereof.

4. A method as recited in claim 1, wherein the metal-oxygen is regenerated with air or oxygen.

5. A method as recited in claim 1, wherein formation of the product hydrocarbon is carried out in a zone reactor.

6. A method as recited in claim 1, wherein the halogenating agent comprises molecular halogen.

7. A method as recited in claim 6, wherein the molecular halogen comprises bromine.

8. A method as recited in claim 1, wherein the halogenating agent comprises an alkyl halide.

9. A method as recited in claim 1, wherein the halogenating agent comprises a solid halide.

10. A method as recited in claim 1, wherein the halogenating agent comprises a hydrogen halide.

11. A method of making a hydrocarbon having a carbon number C_n, where n ≥ 2, comprising:

forming a brominated hydrocarbon by allowing a reactant hydrocarbon having a carbon number C_m, where m < n, to react with a brominating agent;

forming a product hydrocarbon having a carbon number C_n, where n ≥ 2, by allowing the brominated hydrocarbon to contact a metal-oxygen cataloreactant;

recovering the product hydrocarbon; and

regenerating the metal-oxygen cataloreactant.

12. A method as recited in claim 11, wherein the reactant hydrocarbon comprises methane.

13. A method as recited in claim 11, wherein the metal-oxygen cataloreactant is selected from the group consisting of zeolites, doped zeolites, metal oxides, mixed metal oxides, metal oxide-impregnated zeolites, and mixtures thereof.

14. A method as recited in claim 1, wherein the metal-oxygen cataloreactant is regenerated with air or oxygen.

15. A method as recited in claim 11, wherein formation of the product hydrocarbon is carried out in a zone reactor.

16. A method as recited in claim 11, wherein the brominating agent is selected from the group consisting of bromine, alkyl bromides, solid bromides, and hydrogen bromide.

17. A method of making a hydrocarbon having a carbon number C_n, where $n \geq 2$, comprising:

(i) forming an alkyl halide by allowing a reactant alkane having a carbon number C_m, where $m < n$, to react with molecular halogen;

(ii) forming a product hydrocarbon having a carbon number C_n, where $n \geq 2$, by allowing the alkyl halide to contact a metal-oxygen cataloreactant;

(iii) recovering the product hydrocarbon; and

(iv) regenerating the metal-oxygen cataloreactant with air or oxygen.

18. A method as recited in claim 17, wherein the reactant alkane comprises methane.

19. A method as recited in claim 17, wherein the molecular halogen comprises bromine.

20. A method as recited in claim 17, wherein step (i) occurs at an alkane-to-halogen ratio of from 1: 10 to 100 : 1 by volume.

21. A method as recited in claim 19, wherein step (i) occurs at a temperature of from 20 to 900 °C and a pressure of from 0.1 to 200 atm.

22. A method as recited in claim 17, wherein the metal-oxygen cataloreactant is selected from the group consisting of zeolites, doped zeolites, metal oxides, mixed metal oxides, metal oxide-impregnated zeolites, and mixtures thereof.

23. A method as recited in claim 17, wherein steps (i) - (iv) take place in a zone reactor.

24. A method of making a hydrocarbon having a carbon number C_n, where $n \geq 2$, comprising:

(i) forming an alkyl bromide by allowing methane to react with molecular bromine, at a temperature of from 20 to 900 °C, a pressure of from 0.1 to 200 atm, and a methane-to- bromine ratio of from 1:10 to 100:1 by volume;

(ii) forming a product hydrocarbon having a carbon number C_n, where $n \geq 2$, by allowing the alkyl bromide to contact a doped zeolite;

(iii) recovering the product hydrocarbon; and

(iv) regenerating the doped zeolite with air or oxygen; wherein steps (i)- (iv) occur in a zone reactor.

25. A method of making a product hydrocarbon comprising:

reacting a halogenating agent with a reactant hydrocarbon having a carbon number C_m, where $m<n$, to form a halogenated hydrocarbon;

contacting the halogenated hydrocarbon with a metal-omen cataloreactant to catalyze formation of a product hydrocarbon having a carbon number C_n, where $n \geq 2$, while halogenating the metal-oxygen cataloreactant to form a halogenated cataloreactant;

recovering the product hydrocarbon;

reacting the halogenated cataloreactant with oxygen or air to regenerate the metal-oxygen cataloreactant and form a molecular halogen; and

recycling the molecular halogen as the halogenating agent to react with the reactant hydrocarbon.

26. A method as recited in claim 1, further comprising;

forming a hydrogen halide by allowing the halogenated hydrocarbon to contact the metal-oxygen cataloreactant;

trapping halogen from the hydrogen halide with the metal-oxygen cataloreactant; and

recovering the halogen after regenerating the metal-omen cataloreactant.

27. A method as recited in claim 11, further comprising:

forming hydrogen bromide by allowing the brominated hydrocarbon to contact the metal-oxygen cataloreactant;

trapping bromine from the hydrogen bromide with the metal-oxygen cataloreactant; and

recovering the bromine after regenerating the metal-oxygen cataloreactant.

28. A method as recited in claim 17, further comprising:

forming a hydrogen halide by allowing the alkyl halide to contact the metal-oxygen cataloreactant;

2004268935 05 Nov 2010

trapping halogen from the hydrogen halide with the metal-oxygen catalo reacactant; and

recovering the halogen after regenerating the metal-oxygen cataloreactant.

29. A method as recited in claim 25, further comprising:

forming hydrogen bromide by allowing the alkyl bromide to contact the doped zeolite;

trapping bromine from the hydrogen bromide with the doped zeolite; and

recovering the bromine after regenerating the doped zeolite.