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(54) **INTEGRATED PROCESS FOR SYNTHESIZING ALCOHOLS, ETHERS, ALDEHYDES, AND OLEFINS FROM ALKANES**

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Related U.S. Application Data

(63) Continuation of application No. 10/307,789, filed on Dec. 2, 2002, which is a continuation-in-part of application No. 10/208,068, filed on Jul. 29, 2002, now abandoned, which is a continuation-in-part of application No. 10/054,004, filed on Jan. 24, 2002, now Pat. No. 6,486,368, which is a continuation-in-part of application No. 09/951,739, filed on Sep. 11, 2001, now Pat. No. 6,465,696, which is a continuation-in-part of application No. 09/886,078, filed on Jun. 20, 2001, now Pat. No. 6,472,572.

(51) **Int. Cl.**[7] **C07C 45/00**; C07C 47/02

(52) **U.S. Cl.** **568/490**; 568/448; 568/449

(58) **Field of Search** 568/490, 448, 568/449, 469.9, 470

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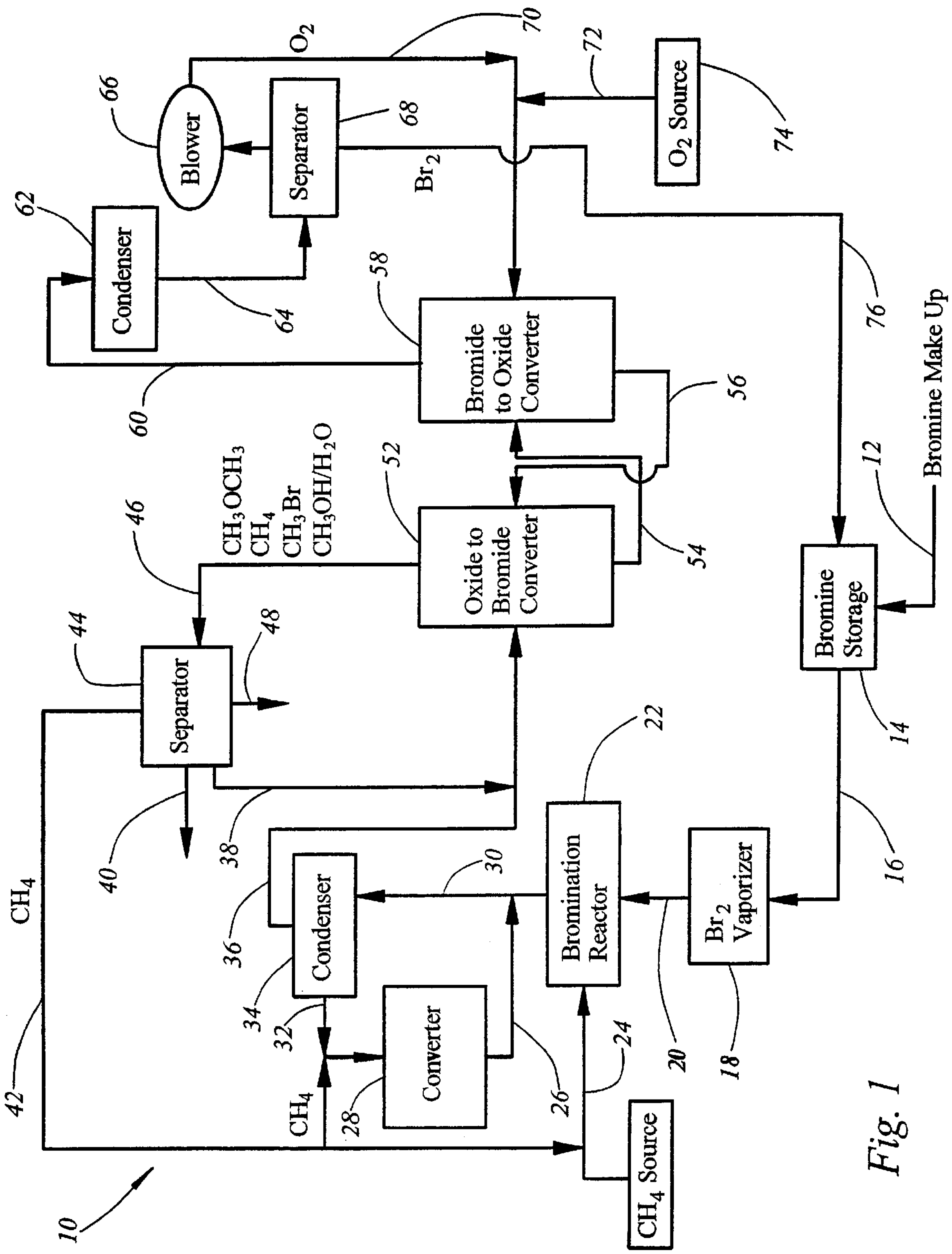
Assistant Examiner—Elvis O. Price

(57) **ABSTRACT**

Alcohols, ethers, aldehydes, and olefins are manufactured from alkanes by mixing an alkane and a halogen selected from the group including chlorine, bromine, and iodine in a reactor to form alkyl halide and hydrogen halide. The alkyl halide only or the alkyl halide and the hydrogen halide are directed into contact with metal oxide to form an alcohol and/or an ether, or an olefin and metal halide. The metal halide is oxidized to form original metal oxide and halogen, both of which are recycled.

20 Claims, 4 Drawing Sheets



10
CH_4 Source
Bromination Reactor
Br_2 Vaporizer
Bromine Storage
Bromine Make Up
Converter
Condenser
Separator
CH_4
Oxide to Bromide Converter
Bromide to Oxide Converter
CH_3OCH_3
CH_4
CH_3Br
CH_3OH/H_2O
Condenser
Separator
Blower
O_2
Br_2
O_2 Source
12
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Fig. 1

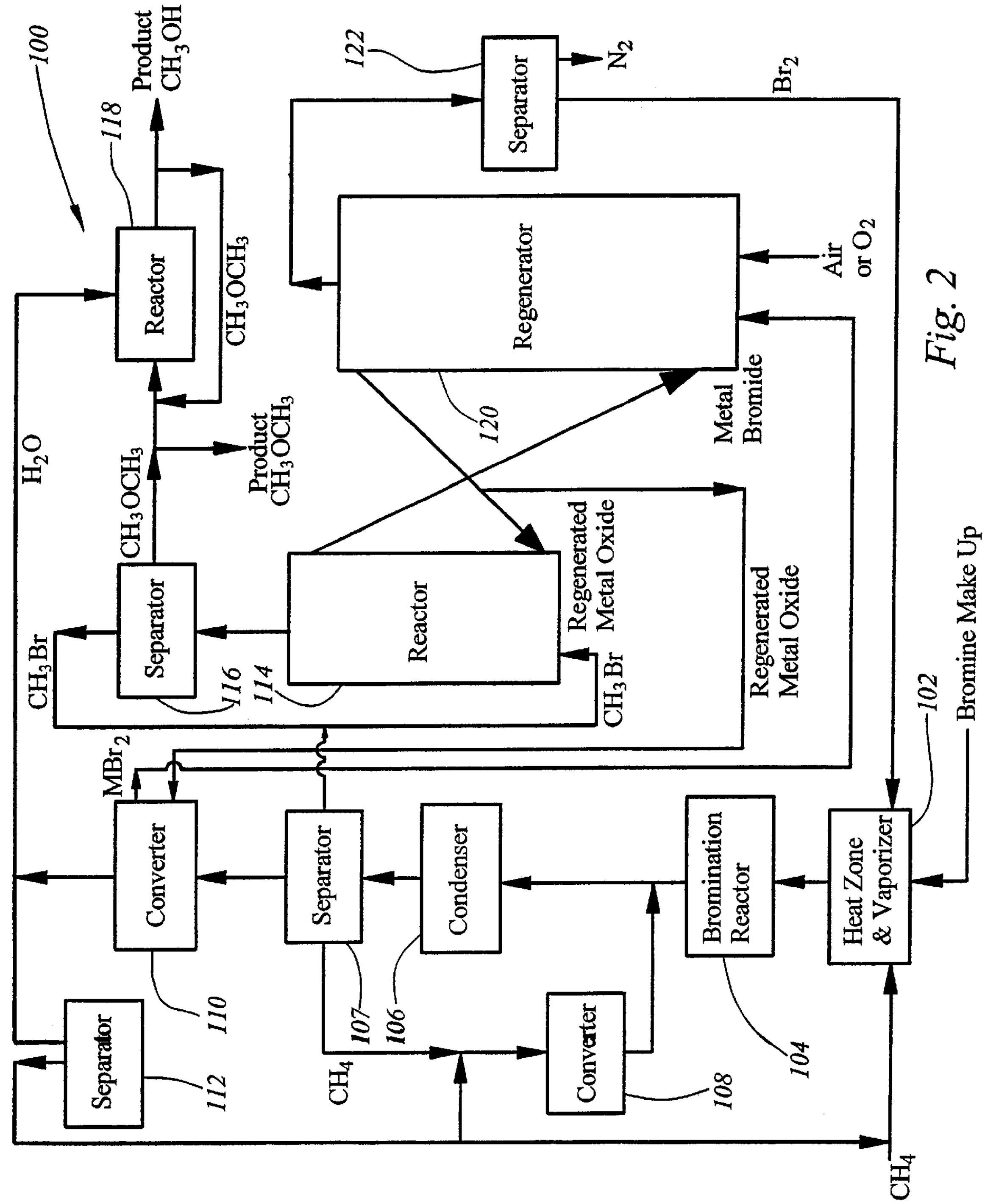

100
Product
CH_3OH
118
Reactor
CH_3OCH_3
H_2O
CH_3OCH_3
Product
CH_3OCH_3
122
Separator
N_2
Br_2
Regenerator
Air
or O_2
120
Metal
Bromide
Regenerated
Metal Oxide
Reactor
Separator
CH_3Br
116
114
CH_3Br
Regenerated
Metal Oxide
MBr_2
Converter
Separator
Condenser
Bromination
Reactor
Heat Zone
& Vaporizer
102
Bromine Make Up
110
107
106
104
Separator
112
CH_4
Converter
108
CH_4

Fig. 2

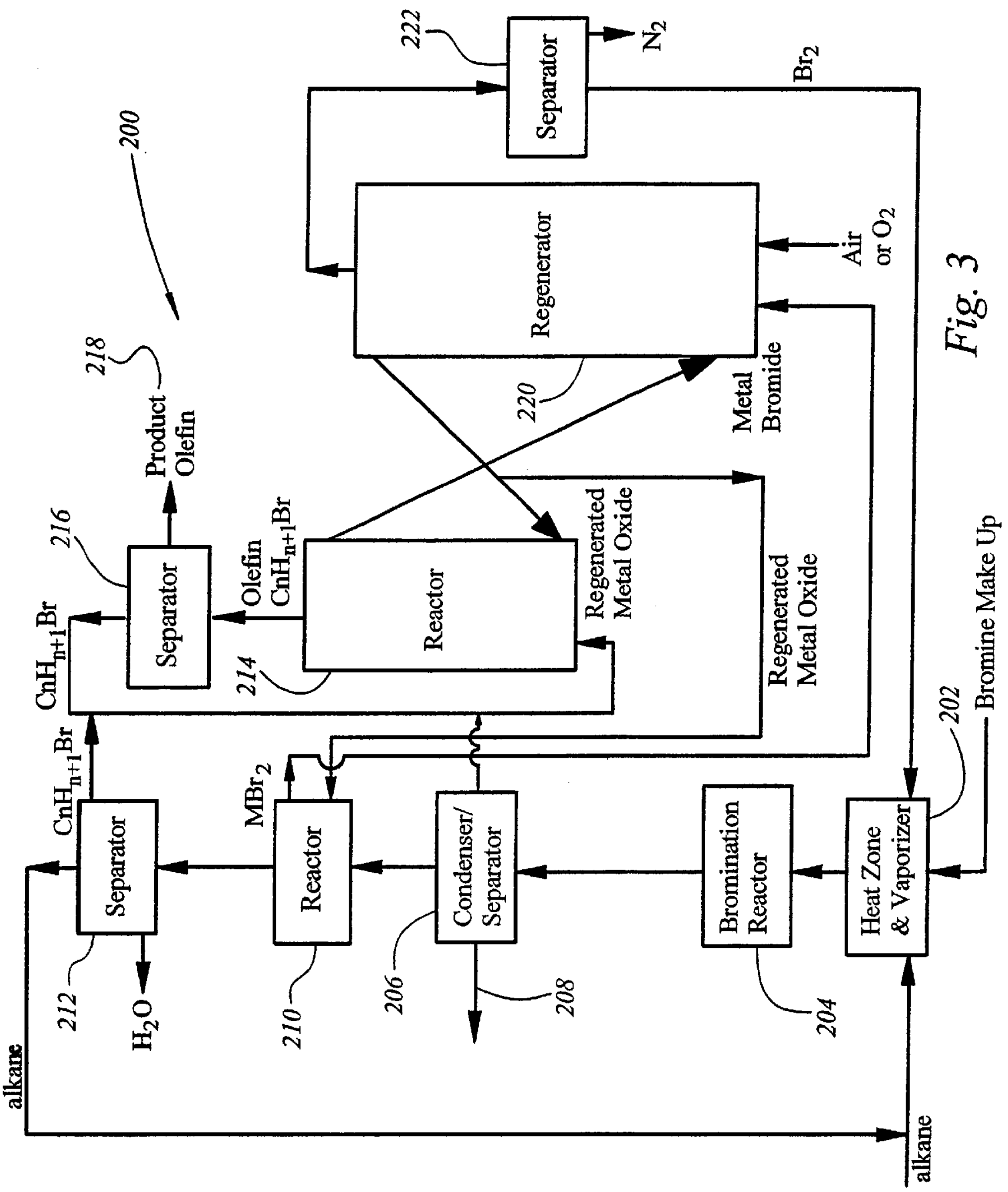
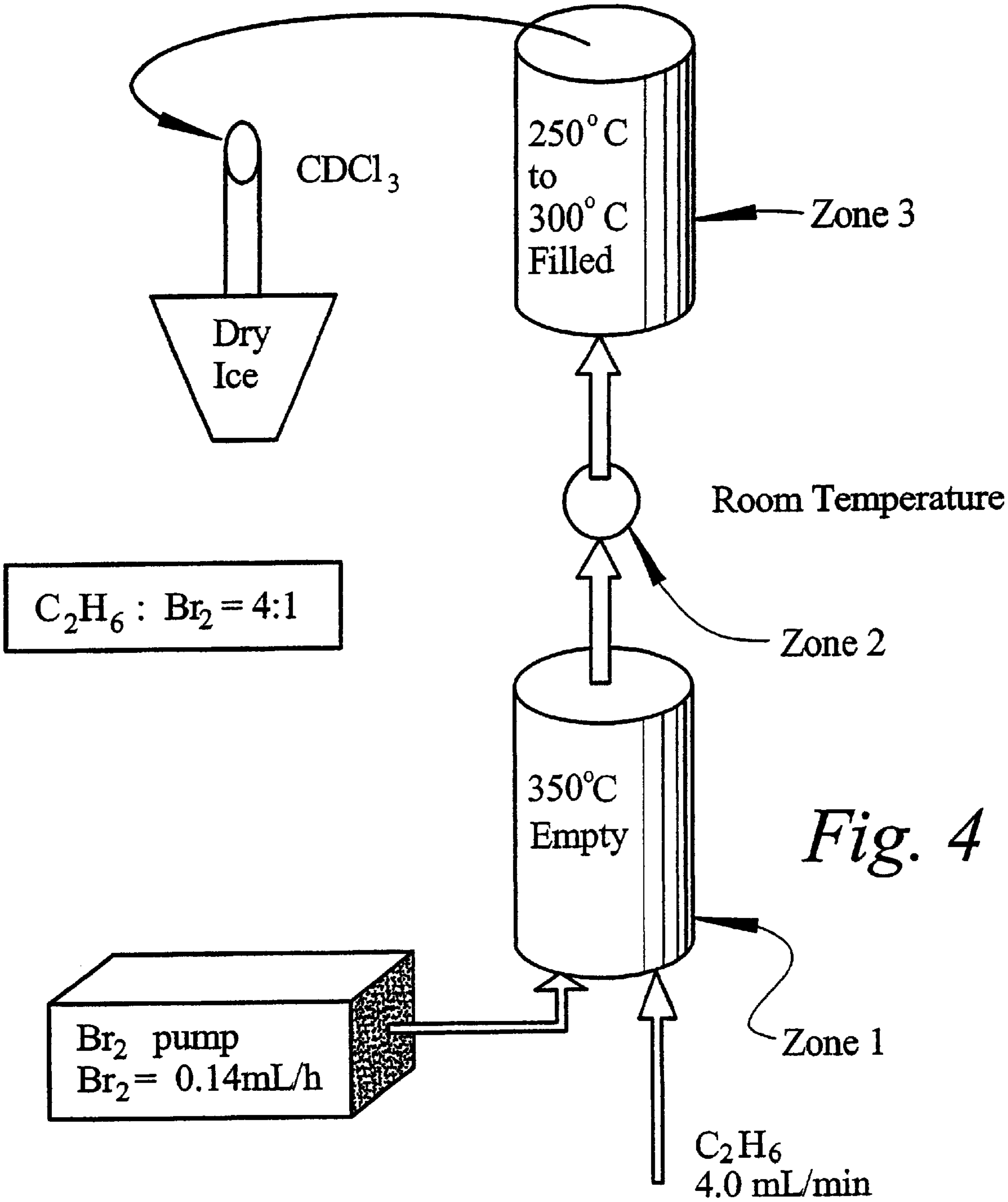

200
222
Separator
N_2
Br_2
Regenerator
Air
or O_2
220
Metal
Bromide
218
Product
Olefin
216
Separator
Olefin
$CnH_{n+1}Br$
Reactor
214
Regenerated
Metal Oxide
Regenerated
Metal Oxide
$CnH_{n+1}Br$
$CnH_{n+1}Br$
Separator
212
H_2O
alkane
MBr_2
Reactor
210
Condenser/
Separator
206
208
Bromination
Reactor
204
Heat Zone
& Vaporizer
202
Bromine Make Up
alkane

Fig. 3



CDCl3
250° C
to
300° C
Filled
Zone 3
Dry
Ice
Room Temperature
C2H6 : Br2 = 4:1
Zone 2
350°C
Empty
Br2 pump
Br2 = 0.14mL/h
Zone 1
C2H6
4.0 mL/min

Fig. 4

INTEGRATED PROCESS FOR SYNTHESIZING ALCOHOLS, ETHERS, ALDEHYDES, AND OLEFINS FROM ALKANES

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation application under 37 C.F.R. §1.63 of application Ser. No. 10/307,789 filed Dec. 2, 2002, which is a CIP application under 37 C.F.R. §1.63 of application Ser. No. 10/208,068 filed Jul. 29, 2002, now abandoned , which is a continuation-in-part application under 37 C.F.R. §1.63 of application Ser. No. 10/054,004 filed Jan. 4, 2002, now U.S. Pat. No. 6,486,368, which is a continuation-in-part of application Ser. No. 09/951,739 filed Sep. 11, 2001, now U.S. Pat. No. 6,465,696, which is a continuation-in-part application of application Ser. No. 09/886,078 filed Jun. 20, 2001, now U.S. Pat. No. 6,472,572.

TECHNICAL FIELD

This invention relates generally to the synthesis of alcohols, ethers, aldehydes, and olefins from alkanes, and more particularly to a method of and apparatus for manufacturing methanol and dimethyl ether from methane; for manufacturing ethanol, diethyl ether, ethyl acetate, and acetaldehyde from ethane; and for converting alkanes to their corresponding olefins.

BACKGROUND OF THE INVENTION

Methane has previously been converted to methanol by the halogenation of methane followed by hydrolysis of the methyl halide to form methanol. For example, gaseous chlorine has been used to chlorinate methane to form chlorinated methane, principally methyl chloride, together with other chlorides, i.e., dichloromethane, trichloromethane and carbon tetrachloride. Alternatively, methane has been subjected to oxychlorination with oxygen and hydrochloric acid to form the foregoing compounds. The chlorinated methanes produced are hydrolyzed in the vapor phase to produce methanol, formaldehyde, formic acid and by-products, including carbon dioxide and hydrochloric acid, depending on the chlorination selectivity. Hydrochloric acid is produced or used in the halogenation of methane by either method and must be recovered, dehydrated by azeotropic distillation and recycled. Corrosion and other problems involved with the handling of chlorine and hydrochloric acid are substantial.

U.S. Pat. No. 3,172,915 granted to Borkowski, et al. is directed to a process for converting methane to methanol. Borkowski discloses the chlorination of methane using ferric chloride at high temperatures to produce chloromethanes and hydrogen chloride. The process requires temperatures in the range of 220–800° C., more preferably 250–450° C., and long residence times, e.g., more than one hour. Further, the process is hindered by the production of a mixture of chlorination products, e.g., chloromethane, dichlbromethane, trichloromethane and carbon tetrachloride, which must be separated before hydrolysis to methanol. Other disadvantages result from the energy required to dry the ferric chloride and from the corrosion and handling problems inherent with hydrochloric acid.

U.S. Pat. No. 5,243,098 granted to Miller discloses another method for converting methane to methanol. In the Miller process, the reaction of methane with cupric chloride produces chloromethane and hydrochloric acid. These intermediates are then reacted with steam and a catalyst containing magnesium oxide to produce methanol and magnesium chloride. Magnesium oxide is regenerated by treatment of the magnesium chloride by-product with air or oxygen. Cupric chloride is regenerated by treatment of the cuprous chloride by-product with air and hydrochloric acid. While these reactions proceed at favorable rates, attrition of the solid reactants, i.e., cupric and magnesium oxide, is significant. Special filters and processes are required to recover and regenerate the reactants in the required particle size. Miller also suggests cupric bromide and magnesium zeolite as alternative reactants. Because of the attrition of the reactants, difficulties associated with the handling of solids, and the special filters and processes required to regenerate the reactants, the Miller process has proved unsatisfactory. U.S. Pat. No. 5,334,777, also granted to Miller, discloses a nearly identical process for converting ethane to ethylene glycol.

U.S. Pat. No. 5,998,679 granted to Jorge Miller, discloses a process for converting alkanes and alkenes to the corresponding lower alkanols and diols. In the method of the invention, a gaseous halogen (bromine) is produced by decomposing a metal halide in a liquid having a melting point below and a boiling point above the decomposition temperature of the metal halide. The preferred liquid is molten hydrated ferric chloride maintained at a temperature between about 37–280° C. The lower alkane or alkene is halogenated in a gas phase reaction with the halogen. The resulting alkyl halide or alkyl dihalide is contacted with a metal hydroxide, preferably an aqueous solution of ferric hydroxide, to regenerate the metal halide and produce the corresponding lower alkanol or diol. Problems with this process include low monohalogenation selectivity, and corrosiveness of the hydrated ferric halides, which may present a containment problem if the process is run at 280° C., where high pressure steam is required to maintain ferric halide hydration. Finally, the process produces a great deal of water and HCl or HBr, all of which are difficult to separate on a large scale from the desired product methanol.

Published international patent application WO 00/07718, naming Giuseppe Bellussi, Carlo Perego, and Laura Zanibelli as inventors, discloses a method for directly converting methane and oxygen to methanol over a metal halide/metal oxide catalyst. This is not a catalyst in the true sense, however, because the reaction involves transfer of halide from a metal halide via reaction with methane to a different metal oxide producing the metal halide and methanol downstream. Eventually the halide is leached and the catalyst loses activity.

Olah, et al. (George A. Olah, et al. *J. Am. Chem. Soc.* 1985, 107, 7097–7105) discloses a method for converting methane to methanol via methyl halides (CH_3Br and CH_3Cl), which are then hydrolyzed to prepare methanol. In the process, CH_3Br and CH_3Cl are hydrolyzed over catalysts with excess steam generating a methanol, water, and a HCl or HBr mixture. The separation of methanol (about 2% by mole) from HCl or HBr and water on an industry scale (2000 tons per day) requires an enormous amount of energy and generates a great deal of aqueous HCl or HBr waste. Aqueous HCl and HBr are very corrosive as well.

SUMMARY OF THE INVENTION

The present invention comprises a process wherein bromine or a bromine-containing compound is used as an intermediate to convert alkanes to alcohols, ethers, aldehydes, or olefins by reaction with oxygen (or air). While the process can be used to convert a variety of alkanes, including methane, ethane, propane, butane, isobutane, pentanes, hexanes, cyclohexane, etc. to their respective alcohols, ethers, aldehydes, or olefins, the conversion of methane to methanol and dimethyl ether is illustrative.

Methane reacts with a halogen selected from the group including chlorine, bromine, and iodine to form a methyl halide and a hydrogen halide, for example CH_3Br and HBr. The reaction may be catalytic or non-catalytic. The methyl bromide reacts with a metal oxide to form a variable mixture of dimethyl ether (DME), water and methanol, and the metal bromide. The metal oxide and molecular bromine are regenerated by reaction of the metal bromide with air and/or oxygen. The regenerated bromide is recycled to react with methane while the regenerated metal oxide is used to convert more methyl halide to methanol and DME, completing the reaction cycle.

The process can be easily carried out in a riser reactor. Compared to the current industrial two step process, in which methane and steam are first converted to CO and H_2 at 800° C. followed by conversion to methanol over a Zn—Cu—Al—O catalyst at approximately 70–150 atmospheres, the process of the present invention operates at roughly atmospheric pressure and relatively low temperatures, thereby providing a safe and efficient process for methanol production.

The present invention operates with solid/gas mixtures at atmospheric pressure. In the process, the hydrogen halide is gaseous, and therefore not as corrosive as when aqueous at high temperatures. The reaction of the halide with an alkane can reach more than 90% selectivity and high conversion to alkane-monohalide. The main side products, alkane dihalides such as CH_2Br_2, can be converted back to the monohalides by reaction with an alkane. The reaction may be catalytic or non-catalytic. Very few by-products are produced.

During operation, most of the halide atoms are trapped in the solid state, making the system less corrosive. Another advantage is that in the process, DME and alcohol (CH_3OH) are not produced as a mixture with excess water. By controlling reaction conditions, almost pure DME and/or methanol is obtained directly so that it is not necessary to separate CH_3OH from water. Finally, in the present process, methane and oxygen do not come into direct contact, resulting in improved safety.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete understanding of the present invention may be had, by reference to the following Detailed Description when taken in connection with the accompanying Drawings, wherein:

FIG. **1** is a schematic illustration of a method of and apparatus for synthesizing alcohols and/or ethers from alkanes comprising a first version of the first embodiment of the invention;

FIG. **2** is a schematic illustration of a method of and apparatus for synthesizing alcohols and/or ethers from alkanes comprising a second version of the first embodiment of the invention;

FIG. **3** is a schematic illustration of a method of and apparatus for synthesizing olefins from alkanes comprising a second embodiment of the invention; and

FIG. **4** is a schematic illustration of a reactor configuration useful in manufacturing acetaldehyde from ethane.

DETAILED DESCRIPTION

Alkanes (methane, ethane, propane, butane, isobutane, pentanes, hexanes, cyclohexane, etc.) react with a molecular halogen selected from the group including chloride, bromine, and iodine to form alkylhalides. The reaction may be catalytic or non-catalytic. Most of the by-product is CH_2Br_2 plus 2 HBr, trace amounts of $CHBr_3$ and CBr_4, which can be catalytically reconverted to CH_3Br by reacting CH_2Br_2, $CHBr_3$, and CBr_4 with CH_4.

Referring to the Drawings, and particularly to FIG. **1**, a method and apparatus **10** for synthesizing alcohols and ethers from alkanes using a halogen selected from the group including chloride, bromine and iodine comprising a first version of the first embodiment of the invention is schematically illustrated. In the operation of the method and apparatus **10**, a halide, for example, bromine is received from a suitable source through a line **12** and is directed to a bromine storage container **14**. As is well known, bromine is easily manufactured from bromide, which is readily available from sea water.

As is also well known, bromine is a liquid at room temperature. Liquid bromine from the storage container **14** is directed through a line **16** to a bromine vaporizer **18** wherein the bromine is converted from the liquid phase to the gas phase. From the vaporizer **18** the gaseous bromine is directed through a line **20** to a reactor **22**.

Methane from a suitable source is directed to the reactor **22** through a line **24**. Within the reactor **22** the methane and the gaseous bromine are mixed together over an appropriate solid catalyst, and the temperature of the mixture is raised to between about 20° C. and about 600° C., thereby converting the methane and the bromine to methyl bromide (CH_3Br) and hydrogen bromide (HBr).

From the reactor **22**, the CH_3Br, the HBr, any unreacted methane and by-products CH_2Br_2, $CHBr_3$, and CBr_4 are directed to a condenser **34** through a line **30**. The by-products CH_2Br_2, $CHBr_3$, and CBr_4 are in the liquid state and are sent through a line **32** to a converter **28** to react with methane. In the converter **28** methane reacts with the by-products CH_2Br_2, $CHBr_3$, and CBr_4 to form CH_3Br. The newly formed CH_3Br and unreacted CH_2Br_2, $CHBr_3$, CBr_4 and methane are sent to the condenser **34** through a line **26** and the line **30**.

From the condenser **34**, gas phase methane, HBr, and CH_3Br are sent to a converter **52**, through a line **36**. In the converter **52** HBr and CH_3Br react with metal oxide to form CH_3OCH_3, CH_3OH, and H_2O, which are sent to a separator **44**, along with unreacted methane and CH_3Br through a line **46**.

In the separator **44**, dimethyl ether and methanol/water are separated as, products and recovered at outlets **40** and **48**, respectively. The methanol is subsequently removed from the water by distillation. CH_3Br is sent back to the converter **52** through the line **38** and the line **36**. Methane from the separator **44** is sent back to the bromination reactor **22** through the line **42** and the line **24**.

In the converter **52**, the original metal oxide is converted to metal bromide and must be regenerated. The metal bromide from the converter **52** is sent to a converter **58** through a line **54** to react with oxygen received from a source **74** through a line **72** to regenerate bromine and metal oxide. The regenerated metal oxide is sent back to the converter **52** through a line **56**, while the bromine and unreacted oxygen are sent to a condenser **62** through a line **60**, after which they are separated in a separator **68**. The liquid bromine is sent to the storage container **14**, while the oxygen is sent to the converter **58** through a blower **66** and a line **70**.

Referring to FIG. **2**, there is shown a method of and apparatus **100** for synthesizing alcohols and ethers from alkanes comprising a second version of the first embodiment of the invention. The method and apparatus **100** can be used with alkanes such as methane, ethane, propane, butane, isobutene, pentanes, hexanes, cyclohexane, etc. The method and apparatus **100** also employs a halide selected from the group including chlorine, bromine, and iodine.

For example, methane and bromine are directed to a heat zone and vaporizer **102** where the bromine is converted from a liquid to a gas and mixed with methane at a temperature above the atmospheric boiling point of bromine. The gas mixture is passed into a bromination reactor **104** containing an appropriate solid catalyst. After the reaction, the mixture is directed to a condenser **106**. The liquid phase contains by-products CH_2Br, $CHBr_3$, and CBr_4, while the gas phase contains bromomethane, HBr, and unreacted methane.

The by-products CH_2Br_2, $CHBr_3$, and CBr_4 are sent to a converter **108** where they react, either catalytically or non-catalytically, with methane to form bromomethane. After the reaction the mixture is sent to the condenser **106**.

The conversion of the by-products CH_2Br_2, $CHBr_3$, and CBr_4 to bromomethane in the converter **108** can be facilitated by the use of an electrophilic catalyst such as $AlBr_3$, SbF_5 etc. which provides a low barrier pathway allowing direct four centered exchange of H and Br. The reaction may be represented as follows:

$$CH_4 + CBr_4 + AlBr_3\ (cat) \xrightarrow{\Delta} CH_3Br + CH_3Br + AlBr_3$$

The overall reaction is isothermic and therefore may be driven by fractional recovery of higher bromides and removal of bromomethane from the reaction mixture, all in the presence of excess methane.

The gas phase mixture from the condenser **106** is passed through a converter **110**, where HBr reacts with the metal oxide to form metal bromide and water. The metal bromide is sent to a regenerator **120** to regenerate metal oxide. From the converter **110**, the water, bromomethane, and methane are separated in a separator **112**. Methane is recycled to the converter **108** and the vaporizer **102**. Bromomethane is sent to the reactor **114**, Water is sent to the reactor **118**.

In the reactor **114**, bromomethane reacts with metal oxide to generate dimethyl ether (DME) and metal bromide. Metal bromide is sent to the regenerator **120**. The mixture of bromomethane and DME from the reactor **114** is sent to a separator **116**. Bromomethane is recycled to the reactor **114**, while DME is obtained as a product or directed to reactor **118**. In the reactor **118** DME reacts with water (from the separator **112**) to form methanol. The reaction may be catalytic or non-catalytic.

In the regenerator **120**, metal bromide from the converter **110** and the reactor **114** reacts with air or oxygen to regenerate metal oxide and bromine. After regeneration the metal oxide is sent to the converter **110** and the reactor **114**, while bromine is sent to the vaporizer **102**. If air is used to provide the oxygen for metal oxide regeneration, nitrogen may be purged from the system through the separator **122**.

Referring to FIG. **3**, there is shown a method and apparatus **200** for synthesizing olefins from alkanes, comprising a second embodiment of the invention. The alkane and a halide selected from the group including chlorine, bromine, and iodine are directed to a heat zone and, when bromine is used, a vaporizer **202**, operating at a temperature above the atmospheric boiling point of bromine, where the now gaseous bromine and methane are allowed to mix. The gas mixture is passed into a bromination reactor **204**. After the reaction, which may be catalytic or non-catalytic, the mixture is directed to a condenser **206**. The heavier alkane muiltibromides (below 1%) are separated for other uses, such as solvent or intermediates for other organic synthesis at an outlet **208**, while the alkane monobromide, HBr, and unreacted alkane are sent to a reactor **210**.

In the reactor **210**, HBr reacts with metal oxide to form metal bromide and water. The metal bromide is sent to a regenerator **220** to be regenerated back to metal oxide. From the reactor **210** the water, alkane monobromide, and alkane are separated in a separator **212**. Unreacted alkane is recycled to the vaporizer **202**, while the alkane monobromide is sent to a reactor **214**. Water is easily separated from the alkane monobromide in the separator **212** as a by-product.

In the reactor **214** alkane monobromide reacts with metal oxide to generate olefin and metal bromide. Metal bromide is sent to the regenerator **220** for regeneration back to metal oxide. The mixture of olefin and unreacted alkane monobromide from the reactor **214** is sent to a separator **216** where they are easily separated due to their widely different boiling points. Unreacted alkane monobromide, if any, is recycled to the reactor **214**, while olefin is obtained as a product.

In the regenerator **220** metal bromide from the reactor **210** and the reactor **214** reacts with air or oxygen to regenerate metal oxide and bromine. After regeneration, metal oxide is sent to the reactor **210** and the reactor **214**, while bromine is sent to the vaporizer **202**. If air is used as the source of oxygen for regeneration of the metal oxide, nitrogen may be purged from the system by a separator **222**.

EXAMPLES

Reaction 1

Catalyst Preparation

Nb_2O_5 (0.8000 g) was mixed with 0.500 ml 96 (w) % H_2SO_4, then the mixture was heated at 110° C. for 4 hours. The temperature increased to 500° C. within 6 hours, and kept at 500° C. for 4 hours. Catalyst C1 was obtained.

ZrO_2 (2.0000 g) was mixed with H_2SO_4 (3.000 ml, 96 (w) %), then the mixture was heated at 110° C. for 4 hours. The temperature increased to 500° C. within 6 hours, and kept at 500° C. for 4 hours. Catalyst C2 was obtained.

Testing

Reaction Conditions

The catalyst was tested at a methane flow of 1.5 ml/minute and Br_2 flow of 0.07 ml/hour. The reaction temperature was 400° C. The reaction was carried out in a micro reactor system. After 6 hours on line reaction, the reaction effluent was analyzed by a GC/MS, and showed a 23% methane conversion with 55% selectivity to CH_3Br.

Summarizing the overall process in Reaction 1:

$$CH_4+Br_2>HBr+CH_3Br+CH_2Br_2+CHBr_3+CBr_4\ cat \quad (1)$$

Reaction 2

Example 1

Reaction on M1

For all of the examples provided above the second stage of the process occurs as follows. After separation of the CH_2Br_2,$CHBr_3$ and CBr_4 products from the gas stream, the CH_3Br, together with the HBr are passed into the next reactor, which contains M1 (50% CuO on ZrO_2) and is maintained at 225° C. Flowing the reactant gases at 10 h^{-1} gives a 96% conversion of CH_3Br+HBr to CH_3OCH_3 and H_2O, or to CH_3OH, or a mixture of CH_3OH, CH_3OCH_3, and H_2O, with 94% selectivity, the remaining product being $CuBr_2/ZrO_2$ and 6%, CO_2. Dimethyl ether and water are converted into methanol if desired in a third reactor containing catalysts.

Example 2

Zr Solution Preparation

$Zr(OCH_2CH_2CH_3)_4$ (70 (w) % in isopropanol, 112.6 ml) was dissolved into acetic acid (275 ml) under stirring. After stirring for 10 minutes, the solution was diluted by water to make a total volume of 500 ml. A solution with a Zr concentration of 0.5M was obtained.

Preparation of M2

$Cu(NO_3)_2$ (0.5M, 7.200 ml) solution was added into $BaBr_2$ (0.5M, 0.800 ml). A clear solution was obtained. To this solution, Zr solution (0.5M) as prepared above was added under stirring. After stirring a few seconds, a gel was obtained. The gel was dried at 110° C. for 4 hours, then heated to 500° C. within 6 hours, and kept at 500° C. for 4 hours. M2 was obtained.

The metal oxide mixture was tested at a CH_3Br flow rate of 1.0 ml/minute at 230° C. In the first half hour, the average CH_3Br conversion was 65%, and the average dimethyl ether selectivity was 90.5%.

Preparation of M3

$Cu(NO_3)_2$ (0.5M, 40.000 ml) solution was added into Zr solution (0.5M, 30.000 ml as prepared above). After stirring a few seconds, a gel was obtained. The gel was dried at 110° C. for 4 hours, then heated to 500° C. within 6 hours, and calcined at 500° C. for 4 hours. M3 was obtained.

Testing

The catalyst C2 (2.0000 g) was loaded in the first reactor (R1). A trap was loaded with 2.000 g of M3. A second reactor (R2) was loaded with M3 (0.8500 g).

Reactants methane and bromine were fed into the first reactor (methane flow of 1.5 ml/minute, Br_2 flow of 0.07 ml/hour). The reaction temperature was 390° C. After reaction in R1 (stabilized by online reaction for more than 8 hours) the resulting mixture was passed through the trap and a mixture of methane and CH_3Br (in a 85:15 molar ratio) was obtained. This gas mixture was fed directly into reactor R2 at 220° C. In the first hour an average CH_3Br conversion of 91% with an average dimethyl ether selectivity of 75% was obtained.

Summarizing the overall process in Reaction 2:

$$CH_3Br+HBr+CuO>CH_3OH+CuBr_2 \quad (2)$$

Possible variations of Reaction 2:

$$2\ HBr+CuO>H_2O+CuBr_2 \quad (2a)$$

$$2\ CH_3Br+CuO>CH_3OCH_3+CuBr_2 \quad (2b)$$

Reaction 3

The solid $CuBr_2/ZrO_2$ was transferred from Reactor 2 to Reactor 3 and treated with O_2 at 300° C. to yield Br_2 and CuO/ZrO_2 at 100% yield and conversion. This reaction may be run at 1000 h^{-1}.

Summarizing the overall process in Reaction 3:

$$CuBr_2/ZrO_2+½O_2>Br_2+CuO/ZrO_2 \quad (3)$$

Overall:

$$CH_4+½O_2>CH_3OH \quad (A)$$

Possible variation:

$$CH_4+½O_2>½CH_3OCH_3+½H_2O \quad (B)$$

A third embodiment of the invention comprises a process for converting ethane to diethyl ether, ethanol, and ethyl acetate which may be carried out as illustrated in FIGS. **1**, **2**, and **3**. In the process, ethane reacts with a halogen selected from the group including chlorine, bromine, and iodine. For example, ethane is reacted with bromine to form bromoethane and HBr. The bromoethane then reacts with metal oxide to form diethyl ether, ethanol, ethyl acetate, and metal bromide. The metal bromide reacts with oxygen or air to regenerate the original metal oxide. In the process, bromine and metal oxide are recycled.

In the ethane/bromine reaction the ethane to bromine ratio is preferably between about 10:1 and about 1:10, and more preferably about 4:1. The temperature range for the ethane/bromine reaction is preferably between about 100° C. and about 500° C. and more preferably between about 300° C. and about 400° C. The ethane/bromine reaction can be either catalytic or non-catalytic, it being understood that if a suitable catalyst is used the selectivity to ethane monobromide or dibromides can be high. The reaction is slightly exothermal and is very easy to control.

The second reaction is preferably carried out at a temperature range of between about 150° C. to about 350° C., and more preferably within a temperature range of about 200° C. to about 250° C. Bromoethane is converted to diethyl ether with 60 to 80% conversion with about 4% selectivity to ethanol and about 3% selectivity to ethyl acetate. Hence, high diethyl ether yield with useful ethanol and ethyl acetate by-products is obtained in a single pass. In the process, there is no direct contact between oxygen and ethane thereby providing a high level of safety. If desired, the diethyl ether can be easily hydrolyzed to ethanol with water over a suitable catalyst.

Example

Part A. Ethane Bromination Reaction

A mixture of ethane (6.0 ml/minute) and bromine (Br_2 0.30 ml/hour) was passed into a reactor (glass tube, ID 0.38", heating zone length 4"), and was heated to 330° C. The effluent was analyzed by GC/MS. 100% bromine conversion with 80% bromoethane selectivity was obtained. The by-product with 20% selectivity was 1,1-dibromoethane. The 1,1-dibromoethane can be converted to bromoethane by reaction with ethane over a catalyst, such as a metal compound or a mixture of metal compounds.

The ethane bromination reaction can also be a catalysis reaction. The catalysts are compounds of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, Sb, Bi, S, Cl, Br, F, Sc, Y, Mg, Ca, Sr, Ba, Na, Li, K, O, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Er, Yb, Lu, and Cs or mixtures thereof. The reaction is preferably carried out at a temperature range of between about 50° C. to about 600° C. The reaction pressure is preferably from about 1 to about 200 atm. The reaction mixture can have a ratio of ethane to bromine from 0.1 to 100.

Part B. The Reaction of Bromoethane with Metal Oxides Zr solution Metal Oxide Preparation

$Zr(OCH_2CH_2CH_3)_4$ (70 (w) % in isopropanol, 112.6 ml) was dissolved into acetic acid (275 ml) under stirring. After stirring for 10 minutes, the solution was diluted with water to make a total volume of 500 ml. A solution with a Zr concentration of 0.5M was obtained.

Preparation of M4

A $Cu(NO_3)_2$ (0.5M, 64.0 ml) solution was added into a Zr solution (0.5M, 64.0 ml) (as prepared above). After stirring for a few seconds, a gel was obtained. The gel was dried at 110° C. for 4 hours, then heated to 500° C. within 6 hours, and calcined at 500° C. for 4 hours. CuO/ZrO_2 metal oxide (M4) was obtained.

Testing

Bromoethane (0.20 ml/hour) and helium (4.0 ml/minute) were passed through a reactor that was packed with 3.0000grams M4, which was heated to 200° C. Within the first hour, an average bromoethane conversion of 70% was observed and diethyl ether in 50 to 60% selectivity was obtained. The ethanol selectivity was about 4% and ethyl acetate selectivity was about 3%.

In the above reaction, the metal oxides can be oxides of the following metals: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, Sb, Bi, S, Cl, Br, F, Sc, Y, Mg, Ca, Sr, Ba, Na, Li, K, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Er, Yb, Lu, and Cs or mixtures thereof.

The reaction can be carried out at a temperature range from about 50° C. to about 600° C. The reaction pressure is preferably from about 1 to about 200 atm. The reaction can be carried out with or without helium. The metal bromide is converted to metal oxide M4 in oxygen or in air to obtain metal oxide and bromine at a temperature range of about 50 to about 700° C. and pressure range from about 1 to about 300 atm.

A fourth embodiment of the invention comprises a process for converting ethane to acetaldehyde, which may S be carried out as illustrated in FIGS. **1**, **2**, and **3**. In the process, ethane is reacted with a halogen selected from the group including chlorine, bromine, and iodine. For example, ethane can be reacted with bromine to form bromoethane and HBr. In the bromination reaction the ethane to bromine ratio is preferably between about 10:1 and about 1:10, and more preferably about 4:1. The temperature range for the bromination reaction is preferably between about 100° C. and about 500° C., and more preferably between about 300° C. and about 400° C.

The bromoethane then reacts with metal oxide to form acetaldehyde and metal bromide. The second reaction is preferably carried out at a temperature range of between about 150° C. and about 350° C., and more preferably at a temperature range of between about 200° C. and about 250° C. The metal bromide is reacted with oxygen or air to regenerate the original metal oxide. In the process, bromine and metal oxide are recycled.

Example

Ethane and bromine were thermally reacted at 350° C. in a first reactor comprising an empty glass tube (ID 0.38", heating zone length 4") by feeding ethane and bromine at a 3.6:1 mol ratio, respectively (ethane=4 ml/min and Br_2=0.14 ml/h). The reaction products comprising the outlet gas were analyzed by gas chromatography (GC) and a flame ionization detector (FID) during the reaction using nitrogen gas as an internal standard. The GC/FID results showed that the reaction achieved 23% ethane conversion. The reaction products comprising the outlet gas were also collected into a $CDCl_3$ solution cooled in a dry-ice acetone bath for nuclear magnetic resonance (NMR) analysis. The NMR results demonstrated a product distribution in mol percents of 76.8% monobromoethane, 19.3% 1,1 dibromoethane, and 3.8% 1,2 dibromoethane.

A second reaction was initiated by directing the reaction products from the first reaction to a second reactor comprising a glass tube (ID 0.38", heating zone length 4") containing 5 g of a metaloxide comprising $CaO/CuO/TiO_2$. The second reaction took place at 250° C. and produced acetaldehyde. After a 1 h reaction the NMR spectrum of products collected in a $CDCl_3$ solution cooled in a dry-ice acetone bath demonstrated that the reaction achieved 100% bromoethane and dibromoethane conversion. The relative distribution of liquid products isolated (in C_2 equivalents) was 59.13% acetaldehyde, 8.53% ethylacetate, 5.36% diethylether, 16.47% ethanol and 10.52% vinylbromide. GC analysis of the gas escaping the $CDCl_3$ trap revealed the formation of CO_2 (15% of brominated ethanes entering the second reactor) and ethylene (15%) as well.

Preparation of the Ti Solution

$Ti[OCH(CH_3)_2]_4$ (97%, 76.7 ml) was dissolved in an oxalic acid solution(56.5 g oxalic acid dissolved in 200 ml distilled water) by heating and stirring for two hours. After two hours, the solution was diluted by water to the total volume of 500 ml. 0.5M Ti Solution was obtained.

Preparation of the Metaloxide

Aqueous solutions comprising 20 ml of 0.5M $Cu(NO_3)_2$ and 20 ml of 0.5M $CaBr_2$ were mixed in 40 ml of 0.5M Ti Solution (prepared as described above). After stirring the mixture 10 minutes it was dried at 120° C. for 4 hours, then heated to 500° C. within 6 hours, and calcined at 500° C. for 4 hours. $CaO/CuO/TiO_2$ was obtained containing 25% each Ca and Cu and 50% Ti in mol percentages.

The Reactor System

Referring to FIG. **4**, ethane bromination and the second reaction were performed in a three-zone reactor. Ethane and bromine were fed into the bottom of reactor zone 1 which was otherwise empty to produce bromoethane. The reactor zones contained the solid metaloxide $CaOCuOTiO_2$ for the oxidation reaction of bromoethane. The reactor zone 2 comprised a glass balloon trap between the two reactors, at room temperature, to reflux and collect any dibromoethane produced in the reactor zone 1. The reactor zone 2 is charged through another inlet for the addition of water to the 2^{nd} reactor system as required.

Example

The reaction of ethyl bromide at 250° C. over 3 g of several times used and regenerated CuO/ZrO2 with ethane as a carrier gas produced acetaldehyde at 21% selectivity (estimated) during the 2^{nd} hour of the reaction period. The distribution of other products was 15% ethanol, 5% diethyl ether, 20% ethyl acetate and 3% butadiene.

Preparation of the Zr Solution

112 ml of $Zr(OCH_2CH_2CH_3)_4$ (70% wt in 1-propanol) solution was dissolved into an oxalic acid solution(56.5 g oxalic acid dissolved in 200 ml distilled water) under stirring. After stirring for 2 hours, the solution was diluted by water to make a total volume of 500 ml. A solution comprising a Zr concentration of 0.5M was obtained.

Preparation of CuO/ZrO_2

Aqueous solutions of 50 ml of 0.5M $Cu(NO_3)_2$ solution and 50 ml of 0.5M Zr solution (prepared as described above) were mixed. After stirring a few seconds, a gel was obtained. The gel was dried at 120° C. for 4 hours, then heated to 500° C. within 6 hours, and calcined at 500° C. for 4 hours. CuO/ZrO_2 was obtained comprising 50% mol Cu and 50% mol Zr.

A fifth embodiment of the invention comprises a process for converting saturated hydrocarbons (alkanes) to their corresponding olefins. For instance, ethane to ethylene, propane to propylene, butane to butene or butadiene, isobutane to isobutene, etc. The process of the fifth embodiment may be carried out as illustrated in FIG. **3**.

In the process, alkane reacts a halogen selected from the group including chlorine, bromine and iodine to form halogenated alkane and hydrogen halide. The halogenated alkane then reacts with metal oxide to form olefin and metal halide. The metal halide reacts with oxygen or air to regenerate the metal oxide. In the process, halogen and metal oxide are recycled.

In the prior art, olefins are made by hydrocarbon thermal cracking. The thermal cracking process also produces saturated hydrocarbons, such as propane, butane, isobutane, pentanes, and hexanes, which are usually difficult to convert to useful materials. For example, ethane can be converted to ethylene by thermal cracking at temperatures over 800° C. in an endothermic reaction, which consumes large amounts of energy, and also generates about 30% by product acetylene (C_2H_2). The acetylene must be hydrogenated back to ethylene which usually leads to over hydrogenation to ethane.

Propane is currently used as fuel, since there presently exists no efficient process that can convert propane to propylene.

There has been research directed at oxidizing alkanes to their corresponding olefins by reacting the alkane with oxygen over catalysts. However, low selectivity and low conversion rates were obtained. The reaction generates large amounts of heat, which can melt the catalyst as well as the reactor. Further, most of these processes involve the direct contact of the alkane with oxygen at high temperature and pressure, which is potentially dangerous.

It is well known that alkanes can easily react with CBr_4, $CHBr_3$, or CH_2Br_2, or react with bromine at low temperatures (below 400° C.) to form alkane monobromides or alkane dibromides. The reaction can be catalytic or non-catalytic. If a suitable catalyst is used, the selectivity to alkane monobromide or dibromide can be very high (more than 95% $CH_3CH_2BrCH_3$ selectivity can be reached). The reaction is slightly exothermal and is very easy to control. In the next reaction, alkane bromide is converted to olefin with 100% conversion (one **5** pass) and selectivity over 95%. Hence, high olefin yield can be obtained in a single pass. In the process, the direct contact of oxygen with alkane is avoided, making the operation safe. A further advantage of the present invention is the virtual elimination of by-products, rendering recovery of the desired olefin substantially easier then the conventional process. An even further advantage of the present invention is the production of the olefin without the production of the corresponding alkyne, thus eliminating the need for partial hydrogenation.

The alkane/bromine reaction is preferably carried out at an alkane to bromine ratio of between about 10:1 and about 1:10, and more preferably at an alkane to bromine ratio of about 4:1. The temperature range of the first reaction is preferably between about 100° C. and about 500° C., and more preferably between about 300° C. and about 400° C. The second reaction is preferably carried out at a temperature of between about 150° C. and about 350° C., and more preferably at a temperature between about 200° C. and about 250° C.

Example

Part A. Alkane Bromination Reaction

Propane Bromination Reaction

A mixture of propane (6.0 ml/minute) and bromine (Br_2 0.30 ml/hour) was passed into a reactor (glass tube ID 0.38", heating zone length 4"), which was heated to 270° C. The effluent was analyzed by GC/MS. 100% bromine conversion with 88.9% 2-bromopropane selectivity and 11.1% 1-bromopropane selectivity were obtained.

This reaction can also be a catalysis reaction. The catalysts are compounds of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, Sb, Bi, S, Cl, Br, F, Sc, Y, Mg, Ca, Sr, Ba, Na, Li, K, O, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Er, Yb, Lu, and Cs or mixtures of such compounds. The reaction can be carried out at a temperature range from about −10° C. to about 600° C. The reaction pressure can be from about 1 to about 200 atm. The reaction mixture can have a ratio of propane to bromine from 0.1 to 100.

Bromination of Isobutane

A mixture of isobutane (6.0 ml/minute) and bromine (Br_2 0.30 ml/hour) was passed into a reactor (glass tube ID 0.38", heating zone length 4"), which was heated to 220° C. The effluent was analyzed by GC/MS. 100% bromine conversion with 97% 2-bromo-2-methyl-propane selectivity was obtained.

This reaction can also be a catalysis reaction. The catalysts are compounds of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, Sb, Bi, S, Cl, Br, F, Sc, Y, Mg, Ca, Sr, Ba, Na, Li, K, O, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Er, Yb, Lu, and Cs or mixtures of such compounds. The reaction can be carried out at a temperature range from about −10° C. to about 600° C. The reaction pressure can be from about 1 to about 200 atm. The reaction mixture can have a ratio of isobutane to bromine from 0.1 to 100.

Part B. The Reaction of Alkane Bromides with Metal Oxides

Preparation of Zr Solution Metal Oxide

$Zr(OCH_2CH_2CH_3)_4$ (70 (w) % in isopropanol, 112.6 ml) was dissolved into acetic acid (275 ml) under stirring. After stirring for 10 minutes, the solution was diluted with water to make a total volume of 500 ml. A solution with a Zr concentration of 0.5M was obtained.

Preparation of M5

$Cu(NO_3)_2$ (0.5M, 4.00 ml) solution was added into $CaBr_2$ (0.5M, 4.00 ml). A clear solution was obtained. To this solution, Zr solution (0.5M, 8.0 ml) as prepared above was added under stirring. After stirring for a few seconds, a gel was obtained. The gel was dried at 110° C. for 4 hours, then heated to 500° C. within 6 hours, and calcined at 500° C. for 4 hours. M5 was obtained.

Preparation of M6

$Cu(NO_3)_2$ (0.5M, 7.20 ml) solution was added into $BaBr_2$ (0.5M, 0.80 ml). A clear solution was obtained. To this solution, Zr solution (0.5M, 8.0 ml) as prepared above was added under stirring. After stirring for a few seconds, a gel was obtained. The gel was dried at 110° C. for 4 hours, then heated to 500° C. within 6 hours, and calcined at 500° C. for 4 hours. M6 was obtained.

Preparation of M7

A $Cu(NO_3)_2$ (0.5M, 8.00ml) solution was added into Zr solution (0.5M, 8.0 ml) as prepared above was added under stirring. After stirring for a few seconds, a gel was obtained. The gel was dried at 110° C. for 4 hours, then heated to 500° C. within 6 hours, and calcined at 500° C. for 4 hours. M7 was obtained.

Testing on M5

2-bromopropane (0.25 ml/hour) and nitrogen (5.0 ml/minute) were passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8701 gram M5 and heated to 200° C. 100% 2-bromopropane conversion with more than 95% propylene selectivity was obtained within the first 40 minutes. As the reaction proceeds, the CuO is converted to $CuBr_2$, and the 2-bromopropane conversion rate decreases. When the reaction was carried out at 180° C., within the beginning 10 minutes, 99% propylene selectivity was reached with 2-bromopropane conversion more than 60%.

1-bromo-2-methyl-propane (0.29 ml/hour) and nitrogen (5.0 ml/minute) were passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8701 gram M5 and heated to 220° C. 100% 1-bromo-2-methyl-propane conversion with more than 96% 2-methyl-propylene selectivity was obtained within the first hour. As the reaction progresses and the CuO is converted to $CuBr_2$, the 2-bromopropane conversion decreases.

1-bromo-propane (0.24 ml/hour) and nitrogen (5.0 ml/minute) were passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8701 gram M5 and heated to 220° C. 100% 1-bromo-propane conversion with more than 90% propylene selectivity was obtained within the first 20 minutes.

2-bromo-2-methyl-propane (0.31 ml/hour) and nitrogen (5.0 ml/minute) were passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8701 gram M5 and heated to 180° C. 100% 2-bromo-2-methyl-propane conversion with more than 96% 2-methyl-propylene selectivity was obtained within the first hour.

Testing on M6

A mixture of 1-bromopropane and 2-bromopropane (volume 1:1) (0.25 ml/hour) and nitrogen (5.0 ml/minute) was passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8980 gram M6 and heated to 200° C. 100% reactant conversion with more than 90% propylene selectivity was obtained within the first 10 minutes.

Testing on M7

A mixture of 1-bromo-2-methyl-propane and 2-bromo-2-methyl-propane (volume 1:1) (0.30 ml/hour) and nitrogen (5.0 ml/minute) were passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8500 gram M7 and heated to 220° C. 100% reactant conversion with more than 95% propylene selectivity was obtained within the first 40 minutes.

The metal oxides used above can be oxides of the following metals: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, B, Al, Ga, In, Ti, Si, Ge, Sn, Pb, P, Sb, Bi, S, Cl, Br, F, Sc, Y, Mg, Ca, Sr, Ba, Na, Li, K, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Er, Yb, Lu, and Cs and mixtures thereof. The reaction can be carried out at a temperature range from about 50° C. to about 600° C. The reaction pressure can be from about 1 to about 200 atm. The reaction can be carried out with or without nitrogen. The metal bromide was converted to metal oxide (M5, M6, and M7) in oxygen or in air to obtain metal oxide and bromine at a temperature range of about 50 to about 700° C. under pressure range from about 1 to about 300 atm.

It will therefore be understood that the method and apparatus of the present invention operates on a continuous or batch basis to convert alkanes to alcohols, ethers, and olefins. The method and apparatus of the present invention operates at relatively low temperatures and at low pressures and is therefore economical to manufacture and use. The bromine, which is utilized in the method and apparatus of the present invention, is continuously recycled. The metal, oxide, which is utilized in the process is continuously refreshed.

Although preferred embodiments of the invention have been illustrated in the accompanying Drawings and described in the foregoing Detailed Description, it will be understood that the invention is not limited to the embodiments disclosed but is capable of numerous rearrangements, modifications, and substitutions of parts and elements without departing from the spirit of the invention.

What is claimed is:

1. A method for converting ethane to acetaldehyde comprising:

providing a quantity of ethane;

providing a quantity of at least one halogen selected from the group consisting of chlorine, bromine, and iodine;

reacting the ethane with the halogen and thereby forming haloethane and hydrogen halide;

directing at least the haloethane into engagement with a metal oxide and thereby forming acetaldehyde and a metal halide.

2. The method according to claim **1** including additional steps of:

oxidizing the metal halide to form the original metaloxide and halogen;

recycling the metaloxide; and

recycling the halogen.

3. The method according to claim **1** wherein the step of reacting the ethane with the halogen is carried out in the presence of excess ethane.

4. The method according to claim **1** wherein the step of reacting ethane with halogen is carried out at a mole ratio of about 4:1 ethane to halogen.

5. The method according to claim **1** wherein the step of directing the haloethane into engagement with a metaloxide is carried out by directing the haloethane into engagement with a metaloxide selected from the group consisting of $CaO/CuO/Ti0_2$ and CUO/ZrO_2.

6. The method according to claim **1** wherein the step of directing the haloethane into engagement with a metaloxide is carried out by directing the bromoethane into engagement with a metaloxide comprising $CaO/CuO/Ti0_2$.

7. The method according to claim **6** wherein the mol ratios of the components of the metaloxide are 25% CaO, 25% CuO, and 50% $Ti0_2$.

8. The method according to claim **1** wherein the step of directing the haloethane into engagement with a metaloxide is carried out by directing the haloethane into a metaloxide comprising CuO/ZrO_2, and wherein the metaloxide comprises a mol ratio of 50% CuO_2 and 50% Zr O_2.

9. A method of converting ethane to acetaldehyde comprising:

providing a first reactor zone;

providing a quantity of ethane;

providing a quantity of a halogen selected from the group consisting of chlorine, bromine, and iodine;

reacting the ethane with the halogen in the first reactor zone and thereby forming haloethane;

providing a second reactor zone;

providing a third reactor zone;

providing a quantity of a metaloxide within the third reactor zone;

directing the haloethane from the first reactor zone through the second reactor zone to the third reactor zone for reaction with the metaloxide therein to form acetaldehyde and metal halide.

10. The method according to claim **9** wherein the reaction of ethane and halogen in the first reactor zone is carried out at about 350° C.

11. The method according to claim **9** wherein the second reactor zone is maintained at room temperature, and wherein any dihaloethane produced during the ethane/halogen reaction in the first reactor zone is refluxed and collected in the second reactor zone.

12. The method according to claim **9** wherein the reaction of the haloethane with the metaloxide in the third reactor zone is carried out at a temperature of between about 250° C. and about 300° C.

13. The method according to claim **9** including additional steps of:

oxidizing the metal halide from the third reactor zone to form the original metaloxide and halogen;

recycling the metaloxide; and

recycling the halogen.

14. The method according to claim **9** wherein the step of reacting the ethane with the halogen is carried out in the presence of excess ethane.

15. The method according to claim **9** wherein the step of reacting ethane with the bromine is carried out at a mole ratio of about 4:1 ethane to halogen.

16. The method according to claim **9** wherein the step of directing the haloethane into engagement with a metaloxide is carried out by directing the haloethane into engagement with a metaloxide selected from the group consisting of $CaO/CuO/Ti0_2$ and CUO/ZrO_2.

17. The method according to claim **9** wherein the step of directing the haloethane into engagement with a metaloxide is carried out by directing the haloethane into engagement with a metaloxide comprising $CaO/CuO/Ti0_2$.

18. The method according to claim **9** wherein the mol ratios of the components of the metaloxide are 25% CaO, 25% CuO, and 50% $Ti0_2$.

19. The method according to claim **9** wherein the step of directing the haloethane into engagement with a metaloxide is carried out by directing the haloethane into a metaloxide comprising CuO/ZrO_2.

20. The method according to claim **19** wherein the metaloxide comprises a mol ratio of 50% CuO_2 and 50% Zr O_2.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,713,655 B2
DATED : March 30, 2004
INVENTOR(S) : Yilmaz et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,
Item [75], Inventors, replace "CA (US) 93317" with -- CA (US) 93117 --.
Item [73], Assignee, add the following:
-- **GRT, Inc.**, The Woodlands, Texas
The Regents of the University of California, Oakland, California --.
Item [56], **References Cited**, U.S. PATENT DOCUMENTS, add the following:

-- 4,513,092	4/23/85	Chu, et al.	502/71
5,087,786	2/11/92	Nubel, et al.	585/500
6,452,058	9/17/02	Schweizer, et al.	570/223 --.

OTHER PUBLICATIONS,
"Selective" reference, replace "MEthane" with -- Methane --.
"Olah, et al.." change to -- Olah, et al. --.
"Antimony Pentafluoride/Graphite CAtalyzed" change to -- Antimony Pentafluoride/ Graphite Catalyzed --.

Column 1,
Line 11, replace "abandoned , which" with -- abandoned, which --.
Line 59, replace "dichlbromethane" with -- dichloromethane --.

Column 4,
Line 43, replace "52 HBr" with -- 52, HBr --.
Line 48, replace "separated as, products" with -- separated as products --.

Column 5,
Line 23, replace "SbF_5" with -- SbF_5, --.
Line 41, replace "to the reactor 114," with -- to the reactor 114. --.

Column 8,
Line 54, replace "Metal Oxides Zr" with -- Metal Oxides. Zr --.

Column 9,
Line 4, replace "3.0000grams" with -- 3.0000 grams --.
Line 24, replace "which may S be" with -- which may be --.
Line 50, replace "by gas chromatography" with -- by gas chromotography --.

Column 11,
Line 34, replace "(one 5 pass)" with -- (one pass) --.
Line 40, replace "easier then" with -- easier than --.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,713,655 B2
DATED : March 30, 2004
INVENTOR(S) : Yilmaz et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 14,
Line 30, replace "CUO/ZrO_2" with -- CuO/ZrO_2 --.
Lines 34 and 36, replace "$Ti0_2$" with -- TiO_2 --.
Line 41, replace "$Zr\ O_2$" with -- ZrO_2 --.

Column 16,
Line 3, replace "$Ti0_2$ and CUO" with -- TiO_2 and CuO --.
Lines 7 and 10, replace "$Ti0_2$" with -- TiO_2 --.
Line 16, replace "$Zr\ O_2$" with -- ZrO_2 --.

Signed and Sealed this

Eighteenth Day of April, 2006

JON W. DUDAS
Director of the United States Patent and Trademark Office