

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

**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°  
5 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, dichloromethane, trichloromethane and carbon tetrachloride, which must be  
10 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. Patent No. 5,243,098 granted to Miller  
15 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  
20 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. Patent No. 5,334,777, also granted to Miller, discloses a nearly identical process for converting ethene to ethylene glycol.

U.S. Patent 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  
5 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  
10 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  
15 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  
20 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  
5 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 ( $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ ), which are then hydrolyzed to prepare  
10 methanol. In the process,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  are hydrolyzed over catalysts with excess steam generating a methanol, water, and a  $\text{HCl}$  or  $\text{HBr}$  mixture. The separation of methanol (about 2% by mole) from  $\text{HCl}$  or  $\text{HBr}$  and water on an industry scale (2000 tons per day) requires an  
15 enormous amount of energy and generates a great deal of aqueous  $\text{HCl}$  or  $\text{HBr}$  waste. Aqueous  $\text{HCl}$  and  $\text{HBr}$  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, 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, or olefins, the conversion of methane to methanol and dimethyl ether is illustrative.

Methane reacts with bromine over a catalyst to form  $\text{CH}_3\text{Br}$  and  $\text{HBr}$ .  $\text{CH}_3\text{Br}$  and  $\text{HBr}$  react 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 bromine is recycled to react with methane while the regenerated metal oxide is used to convert more methyl bromide and  $\text{HBr}$  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<sub>2</sub> 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  
5 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  
10 hydrogen halide is gaseous, and therefore not as corrosive as when aqueous at high temperatures. The reaction of Br<sub>2</sub> with an alkane can reach more than 90% selectivity and high conversion to alkane-monobromide. The main side products, alkane dibromides such as CH<sub>2</sub>Br<sub>2</sub>,  
15 can be converted back to the monobromides by reaction with an alkane over another catalyst. Very few by-products are produced.

During operation, most of the Br atoms are trapped in the solid state, making the system less corrosive.  
20 Another advantage is that in the process, DME and alcohol (CH<sub>3</sub>OH) 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  $\text{CH}_3\text{OH}$  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  
5 accompanying Drawings, wherein:

FIGURE 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;

10 FIGURE 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; and

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

**DETAILED DESCRIPTION**

Alkanes (methane, ethane, propane, butane, isobutane, pentanes, hexanes, cyclohexane etc.) react with molecular bromine over a catalyst composed of all possible metal compounds and mixtures thereof to form alkylbromides. For  $\text{CH}_4$  (although the process may be applied to higher alkanes as well), the process of the present invention can convert more than 50%  $\text{CH}_4$  to  $\text{CH}_3\text{Br}$  and  $\text{HBr}$ , with selectivity higher than 90%. Most of the by-product is  $\text{CH}_2\text{Br}_2$  plus 2  $\text{HBr}$ , trace amounts of  $\text{CHBr}_3$  and  $\text{CBr}_4$ , which can be catalytically reconverted to  $\text{CH}_3\text{Br}$  by reacting  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$  with  $\text{CH}_4$ .

Referring to the Drawings, and particularly to Figure 1, a method and apparatus 10 for synthesizing alcohols and ethers from alkanes using bromine comprising a first version of the first embodiment of the invention is schematically illustrated. In the operation of the method and apparatus 10, bromine is received from a suitable source through a line 12 and is directed to a bromine storage container 14. For example, bromine is easily manufactured from bromide, which is readily available from sea water.

As is 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 ( $\text{CH}_3\text{Br}$ ) and hydrogen bromide ( $\text{HBr}$ ).

From the reactor 22, the  $\text{CH}_3\text{Br}$ , the  $\text{HBr}$ , any unreacted methane and by-products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$  are directed to a condenser 34 through a line 30. The by products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$  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  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$  to form  $\text{CH}_3\text{Br}$ . The newly formed  $\text{CH}_3\text{Br}$  and unreacted  $\text{CH}_2\text{Br}_2$ ,

$\text{CHBr}_3$ ,  $\text{CBr}_4$  and methane are sent to the condenser 34 through a line 26 and the line 30.

From the condenser 34 gas phase methane,  $\text{HBr}$ , and  $\text{CH}_3\text{Br}$  are sent to a converter 52 through a line 36. In  
5 the converter 52  $\text{HBr}$  and  $\text{CH}_3\text{Br}$  react with metal oxide to form  $\text{CH}_3\text{OCH}_3$ ,  $\text{CH}_3\text{OH}$ , and  $\text{H}_2\text{O}$ , which are sent to a separator 44 along with unreacted methane and  $\text{CH}_3\text{Br}$  through a line 46.

In the separator 44 dimethyl ether and  
10 methanol/water are separated as products and recovered at outlets 40 and 48, respectively. The methanol is subsequently removed from the water by distillation.  $\text{CH}_3\text{Br}$  is sent back to the converter 52 through the line 38 and the line 36. Methane from the separator 44 is  
15 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  
20 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  
5 sent to the storage container 14, while the oxygen is sent to the converter 58 through a blower 66 and a line 70.

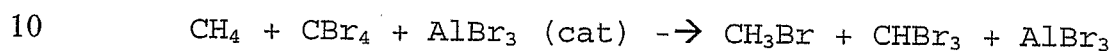
Referring to Figure 2, there is shown a method of and apparatus 100 for synthesizing alcohols and ethers  
10 from alkanes comprising a second version of the first embodiment of the invention. Methane and bromine are directed to a heat zone and vaporizer 102 where the bromine is converted from a liquid to a gas and mixed with methane at a temperature above the atmospheric  
15 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 condenser a 106. The liquid phase contains by products  $\text{CH}_2\text{Br}$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$ , while the gas phase  
20 contains bromomethane,  $\text{HBr}$ , and unreacted methane.

The by products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$  are sent to a converter 108 where they react with methane to form

bromomethane. After the reaction the mixture is sent to the condenser 106.

The conversion of the by products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$  to bromomethane in the converter 108 is facilitated by the use of an electrophilic catalyst such as  $\text{AlBr}_3$ ,  $\text{SbF}_5$ , etc. which provides a low barrier pathway allowing direct four centered exchange of H and Br. The reaction may be represented as follows:

$\Delta$



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.

15      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, 20 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.

5 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) over a catalyst to  
10 form methanol.

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  
15 110 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 Figure 3, there is shown a method and  
20 apparatus 200 for synthesizing olefins from alkanes, which have more than two carbon atoms in their molecular structure, comprising a second embodiment of the

invention. The alkane and bromine are directed to a heat zone and vaporizer 202, operating at a temperature above the atmospheric boiling point of bromine, where the now gaseous bromine and methane are allowed to mix.

5 The gas mixture is passed into a bromination reactor 204, which contains an appropriate solid catalyst. After the reaction the mixture is directed to a condenser 206. The heavier alkane multibromides (below 1%) are separated other uses, such as solvent or

10 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

15 to a regenerator 220 to be regenerated back to metal oxide. From the converter 210 the water, alkane monobromide, and alkane are separated in a separator 212. Unreacted alkane is recycled to a vaporizer 202, while the alkane monobromide is sent to a reactor 214.

20 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 wide different boiling points. Unreacted alkane monobromide, if any, is recycled to the reactor 214, while olefin is obtained as a product.

10 In the regenerator 220 metal bromide from the converter 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 15 202. 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**

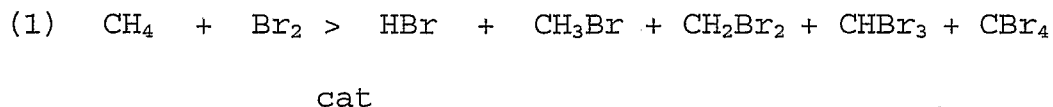
- 5     $\text{Nb}_2\text{O}_5$  (0.8000g) was mixed with 0.500ml 96(w)%  $\text{H}_2\text{SO}_4$ , then the mixture was heated at 110°C for 4 hours. The temperature increased to 500°C within 6 hours, and kept at 500°C for 4 hours. Catalyst C1 was obtained.
- 10    $\text{ZrO}_2$  (2.0000g) was mixed with  $\text{H}_2\text{SO}_4$  (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.

##### 15   **Testing**

Reaction conditions:

- The catalyst was tested at a methane flow of 1.5ml/minute and  $\text{Br}_2$  flow of 0.07ml/hour. The reaction temperature was 400°C. The reaction was carried out in
- 20   a micro reactor system. After 6 hours on line reaction, the reaction effluent was analyzed by a GC/MS. A methane conversion of 24%(mol) with 95%  $\text{CH}_3\text{Br}$  was obtained.

Summarizing the overall process in *Reaction 1*:



5

Reaction 2:

Example 1

Reaction on M1

For all of the examples provided above the second stage  
10 of the process occurs as follows. After separation of  
the  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$  and  $\text{CBr}_4$  products from the gas stream,  
the  $\text{CH}_3\text{Br}$ , together with the  $\text{HBr}$  are passed into the next  
reactor, which contains M1 (50%  $\text{CuO}$  on  $\text{ZrO}_2$ ) and is  
maintained at  $225^\circ \text{C}$ . Flowing the reactant gases at 10  
15  $\text{h}^{-1}$  gives a 96% conversion of  $\text{CH}_3\text{Br} + \text{HBr}$  to  $\text{CH}_3\text{OCH}_3$  and  
 $\text{H}_2\text{O}$ , or to  $\text{CH}_3\text{OH}$ , or a mixture of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$ , and  $\text{H}_2\text{O}$ ,  
with 94% selectivity, the remaining product being  
 $\text{CuBr}_2/\text{ZrO}_2$  and 6%  $\text{CO}_2$ . Dimethyl ether and water are  
converted into methanol if desired in a third reactor  
20 containing catalysts.

**Example 2.****Zr solution preparation**

$\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$  (70(w)% in isopropanol, 112.6 ml) was dissolved into acetic acid (275 ml) under stirring.

- 5 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**

- 10  $\text{Cu}(\text{NO}_3)_2$  (0.5M, 7.200ml) solution was added into  $\text{BaBr}_2$  (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  
15 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  $\text{CH}_3\text{Br}$  flow rate of 1.0 ml/minute at 230°C. In the first half hour, the average  $\text{CH}_3\text{Br}$  conversion was 65%, and the average  
20 dimethyl ether selectivity was 90.5%.

### Preparation of M3

Cu(NO<sub>3</sub>)<sub>2</sub> (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  
5 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.

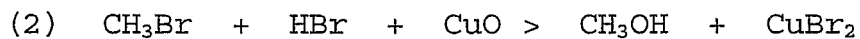
### Testing

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

Reactants methane and bromine were fed into the  
15 first reactor (methane flow of 1.5 ml/minute, Br<sub>2</sub> 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<sub>3</sub>Br  
20 (containing 20% mol of CH<sub>3</sub>Br) was obtained. This gas mixture was fed directly into reactor R2 at 220°C. In the first hour an average CH<sub>3</sub>Br conversion of 91% with an

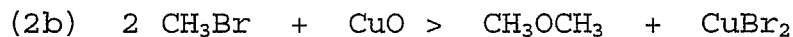
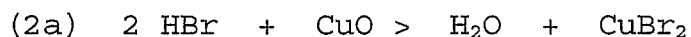
average dimethyl ether selectivity of 75% was obtained.

Summarizing the overall process in *Reaction 2*:



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Possible variations of *Reaction 2*:

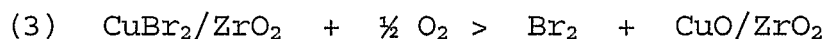


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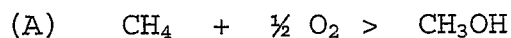
**Reaction 3:**

The solid  $\text{CuBr}_2/\text{ZrO}_2$  was transferred from Reactor 2 to Reactor 3 and treated with  $\text{O}_2$  at  $300^\circ \text{C}$  to yield  $\text{Br}_2$  and  $\text{CuO}/\text{ZrO}_2$  at 100% yield and conversion. This reaction may  
15 be run at  $1000 \text{ h}^{-1}$ .

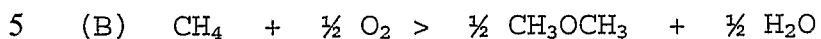
Summarizing the overall process in *Reaction 3*:



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Overall:

## Possible variation:



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  
10 illustrated in Figures 1, 2, and 3. In the process, ethane reacts with bromine to form bromomethane 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  
15 regenerate the original metal oxide. In the process, bromine and metal oxide are recycled.

It is well known that ethane can easily react with bromine at low temperatures (below 400°C) to form bromoethane or ethane dibromides. If a suitable  
20 catalyst is used, the selectivity to ethane monobromide or dibromides is high. The reaction is slightly exothermal and is very easy to control. In the next

reaction, bromoethane is converted to diethyl ether with  
60 to 80% conversion and selectivity over 80% with about  
4% selectivity to ethanol and about 3% selectivity to  
ethyl acetate. Hence, high diethyl ether yield with  
5 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  
10 suitable catalyst.

EXAMPLE**Part A. Ethane Bromination Reaction**

A mixture of ethane (6.0ml/minute) and bromine (Br<sub>2</sub>  
5 0.30ml/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-  
10 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  
15 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,  
20 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.**

**5 Zr solution metal oxide preparation**

Zr(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> (70(w)% in isopropanol, 112.6 ml) was dissolved into acetic acid (275ml) under stirring. After stirring for 10 minutes, the solution was diluted with water to make a total volume of 500ml. A solution with a  
10 Zr concentration of 0.5M was obtained.

**Preparation of M4**

A Cu(NO<sub>3</sub>)<sub>2</sub> (0.5M, 64.0ml) solution was added into a Zr solution (0.5M, 64.0ml) (as prepared above). After  
15 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<sub>2</sub> metal oxide (M4) was obtained.

### Testing

Bromoethane (0.20ml/hour) and helium (4.0ml/minute) were passed through a reactor that was packed with 3.0000 grams M4, which was heated to 200°C. Within the first 5 hour, an average bromoethane conversion of 70%, with diethyl ether 84 to 90% 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 10 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.

15

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 20 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 300atm.

A fourth 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 third embodiment may be carried out as illustrated in Figures 3.

10 In the process, alkane reacts with  $\text{CBr}_4$ ,  $\text{CHBr}_3$ , or  $\text{CH}_2\text{Br}_2$ , or reacts with bromine to form brominated alkanes and  $\text{HBr}$ . The brominated alkane then reacts with metal oxide to form olefin and metal bromide. The metal bromide reacts with oxygen or air to regenerate the metal oxide. In the process, bromine 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  
5 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  
10 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  
15 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  
20 temperatures (below 400°C) to form alkane monobromides or alkane dibromides. If a suitable catalyst is used, the selectivity to alkane monobromide or dibromide can

be very high (more than 95%  $\text{CH}_3\text{CH}_2\text{BrCH}_3$  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 byproducts,  
10 rendering recovery of the desired olefin substantially easier than 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  
15 hydrogenation.

EXAMPLE

## Part A. Alkane bromination reaction

## Propane bromination reaction

5 A mixture of propane (6.0ml/minute) and bromine ( $\text{Br}_2$  0.30ml/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  
10 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,  
15 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  
20 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 (6.0ml/minute) and bromine ( $\text{Br}_2$  0.30ml/hour) was passed into a reactor (glass tube ID 0.38", heating zone length 4"), which was heated to 5 220°C. The effluent was analyzed by GC/MS. 100% bromine conversion with 99% 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, 10 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 15 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<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> (70(w)% in isopropanol, 112.6 ml) was  
5 dissolved into acetic acid (275ml) under stirring. After  
stirring for 10 minutes, the solution was diluted with  
water to make a total volume of 500ml. A solution with a  
Zr a concentration of 0.5M was obtained.

**10 Preparation of M5**

Cu(NO<sub>3</sub>)<sub>2</sub> (0.5M, 4.00ml) solution was added into CaBr<sub>2</sub>  
(0.5M, 4.00ml). A clear solution was obtained. To this  
solution, Zr solution (0.5M, 8.0ml) as prepared above  
was added under stirring. After stirring for a few  
15 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<sub>3</sub>)<sub>2</sub> (0.5M, 7.20ml) solution was added into BaBr<sub>2</sub> (0.5M, 0.80ml). A clear solution was obtained. To this solution, Zr solution (0.5M, 8.0ml) as prepared above  
5 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.

**10 Preparation of M7**

A Cu(NO<sub>3</sub>)<sub>2</sub> (0.5M, 8.00ml) solution was added into Zr solution (0.5M, 8.0ml) 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  
15 heated to 500°C within 6 hours, and calcined at 500°C for 4 hours. M7 was obtained.

**Testing on M5**

2-bromopropane (0.25ml/hour) and nitrogen (5.0ml/minute) were passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8701gram 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<sub>2</sub>, 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 the 60%.

1-bromo-2-methyl-propane (0.29ml/hour) and nitrogen (5.0ml/minute) were passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8701gram 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<sub>2</sub>, the 2-bromopropane conversion decreases.

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

2-bromo-2-methyl-propane (0.31ml/hour) and nitrogen (5.0ml/minute) were passed through a reactor (glass tube  
10 ID 0.38", heating zone length 4") that was packed with 0.8701gram 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.

15

#### Testing on M6

A mixture of 1-bromopropane and 2-bromopropane (volume 1:1) (0.25ml/hour) and nitrogen (5.0ml/minute) was passed through a reactor (glass tube ID 0.38", heating  
20 zone length 4") that was packed with 0.8980gram 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

5 A mixture of 1-bromo-2-methyl-propane and 2-bromo-2-methyl-propane (volume 1:1) (0.30ml/hour) and nitrogen (5.0ml/minute) were passed through a reactor (glass tube ID 0.38", heating zone length 4") that was packed with 0.8500gram M7 and heated to 220°C. 100% reactant  
10 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,  
15 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 and mixtures thereof. The reaction can be carried out at a temperature range  
20 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 300atm.

5

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  
10 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,  
15 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  
20 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.

**THE CLAIMS**

1. A method for converting methane to methanol comprising:

providing a quantity of methane;

5 providing a quantity of bromine;

reacting the methane with the bromine and thereby forming bromomethane, hydrogen bromide, and by products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$ ;

10 reacting the by products with methane in the presence of an electrophilic catalyst to form bromomethane;

directing the methyl bromide and the hydrogen bromide into engagement with a metal oxide catalyst and thereby forming methanol and a metal bromide;

15 oxidizing the metal bromide to form the original metal oxide and bromine;

recycling the metal oxide; and

recycling the bromine.

20 2. The method according to claim 1 wherein the step of reacting the by products with methane is carried out in the presence of excess methane.

3. The method according to claim 1 wherein the electrophilic catalyst is selected from the group including  $\text{AlBr}_3$  and  $\text{SbF}_5$ .

5 4. The method according to claim 1 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine ratio from about 1:10 to about 100:1 (by mole).

10

5. The method according to claim 1 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine ratio from about 1:1 to about 10:1 (by mole).

15

6. The process according to claim 1 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine ratio from about 1:1 to about 5:1 (by mole).

20

7. The method according to claim 1 wherein the step of mixing the methane and the bromine is carried out at a temperature of between about 20°C and about 400°C.

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8. The process according to claim 1 wherein the step of mixing the methane and the bromine to form the methyl bromide and hydrogen bromide and the step of contacting the methyl bromide and the hydrogen bromide with a metal oxide are carried out continuously.

9. The process according to claim 1 wherein the step of mixing the methane and the bromine to form the methyl bromide and hydrogen bromide and the step of contacting the methyl bromide and the hydrogen bromide with a metal oxide are carried out in a batch reaction.

10. The method according to claim 1 wherein the step of oxidizing the metal bromide to form the original metal oxide catalyst and bromine, the step of recycling the metal oxide, and the step of recycling the bromine are carried out continuously.

11. The method according to claim 1 wherein the step of oxidizing the metal bromide to form the original metal oxide catalyst and bromine, the step of recycling the metal oxide, and the step of recycling the bromine  
5 are carried out in a batch reaction.

12. An apparatus for converting methane to methanol and/or ether comprising:

a first reactor;

means for directing methane and bromine into  
5 the reactor to produce bromomethane, hydrogen bromide,  
and by products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$ ;

a second reactor;

means for directing at least the by products  
and methane into the second reactor for reaction in the  
10 presence of an electrophilic catalyst to form  
bromomethane;

a reaction bed comprising a solid metal oxide;

means for directing bromomethane and hydrogen  
bromide from the first and second reactors into contact  
15 with the metal oxide to form methanol and/or ether and  
metal bromide;

means for oxidizing the metal bromide to form  
the original metal oxide and bromine; and

means for recycling the original metal oxide  
20 and the bromine.