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(54) Title: METHYL HALIDES AND METHYL ALCOHOL FROM METHANE

(57) Abstract

Solid acidic or metal catalyst-promoted halogenation of methane to produce methyl monohalides in high selectivity. Concurrent or simultaneous hydrolysis provides methyl alcohol and/or dimethyl ether in good yields.

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METHYL HALIDES AND METHYL
ALCOHOL FROM METHANE

Technical Field

5   This invention relates to solid acidic or metal
catalyst-promoted halogenation of methane to produce
methyl monohalides in high selectivity. Concurrent or
simultaneous hydrolysis provides methyl alcohol and/or
10   dimethyl ether in good yields.
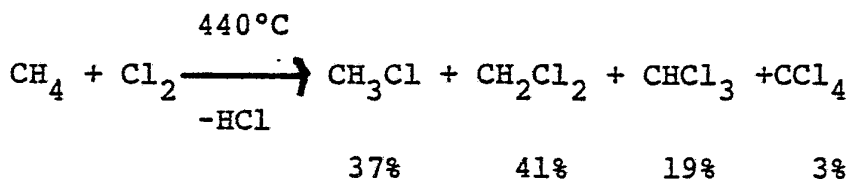
Background Art

         The selective conversion of methane into its
15   monofunctional derivatives, such as methyl halides or
methyl alcohol, is highly desirable, but in practice has
not been achieved on any practical basis.

         The chlorination of methane is an industrial
20   process practiced on a large scale. The reaction is a
strongly exothermic one which takes place via free
radicals and is generally conducted without supplying heat
and usually in the absence of a catalyst at 400-450°C
under slightly elevated pressures. The chlorination is
25   normally thermally initiated via homolysis of chlorine
molecules to chlorine atoms; the process can also be
operated photochemically. For surveys of these processes,
it is appropriate to refer to F. Asinger "Paraffins.
Chemistry and Technology", Pergamon Press, New York, 1968;
30   M. L. Poutsma "Methods in Free Radical Chemistry", Vol.
II, E.S. Huyser, Ed., M. Dekker, New York, 1969; and R.
Weissermel and H. J. Arpe "Industrial Organic Chemistry",
Verlag Chemie, 1978, pp. 46-47. By these reactions, all
of the possible chlorinated methanes are usually formed
35   together when an equimolar Cl_2/CH_4 ratio is employed:

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$$CH_4 + Cl_2 \xrightarrow[-HCl]{440°C} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

$$\phantom{CH_4 + Cl_2 \xrightarrow{} CH_3Cl +} 37\% \quad 41\% \quad 19\% \quad 3\%$$

If methyl chloride is the preferred product, a large
excess of methane (approx. tenfold) must be used, as
methyl chloride is more rapidly chlorinated than methane
under free radical conditions. There are normally many
by-products of the chlorination of methane, such as
hexachloroethane and small amounts of trichloroethylene.

Methyl alcohol is increasingly important not only
as a chemical raw material and building block for such
products as formaldehyde, acetic acid, vinyl acetate,
ethylene glycol and others, but also via its condensation
reactions to give gasoline or hydrocarbons, such as
olefins, aromatics and the like. Its direct use as a
transportation fuel is also gaining importance. A whole
scope of so-called C_1 chemistry is based primarily on
methyl alcohol.

Methyl alcohol, once produced from wood
fermentation (i.e., wood alcohol), is, at the present
time, nearly exclusively produced from CO and H_2
(synthesis gas) derived from coal or natural gas. Coal or
methane first must be converted in an energy consuming
step into syn-gas, which is then, in a second energy
consuming step under pressure and generally forcing
conditions, converted into methyl alcohol. Clearly,
direct oxidative conversion of methane into methyl alcohol
would be highly desirable. Despite continued efforts no
such process was, however, previously achieved on a
practical scale.

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The oxidation of methane generally is not
selective. In the past, many attempted oxidations
concentrated on manufacturing formaldehyde from methane.
The low rate of reaction of CH_4 at temperatures below
5 600°C coupled with the high rate of decomposition of
formaldehyde above 600°C is probably the reason that no
industrial process has been developed to date.
Decomposition of formaldehyde could only be avoided be
extremely short residence times. Such a process has been
10 recently described involving partial oxidation of methane
to methyl alcohol and formaldehyde. The residence time is
1.55×10^{-3} sec. and the pressure 60 atm., respectively
(Huels). However, oxidation of methane, similarly to
chlorination, is free radical chain reaction, which
15 explains the observed lack of selectivity.

I have previously described in the Journal of the
American Chemical Society, Vol. 95, 7686 (1973) that,
under specific conditions, alkanes can undergo
20 electophilic chlorination and chlorinolysis. With a
SbF_5 catalyst in SO_2ClF solution at -78° or at room
temperature with a reaction time of 24 hours, methane was
transformed qualitatively to methyl chloride. No
practical yields were obtained. $AlCl_3$ catalyst gave
25 under similar conditions 1% methyl chloride. These
reactions clearly did not represent a practical method for
the chlorination of methane.

Summary and Description of the Invention

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The present invention relates to a process for
the selective halogenation of methane to produce methyl
halides and through their hydrolysis methyl alcohol and/or
dimethyl ether.

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The Catalysts

Either (i) solid strongly acidic catalysts,
including strong Bronsted or conjugated Lewis-Bronsted
5   superacid catalysts, or (ii) supported Group VIII metal
(particularly platinum and palladium) catalysts are
capable of catalyzing the gas-phase halogenation of
methane predominantly to methyl monohalides in 85 to 99%
selectivity. Subsequent or concurrent catalytic
10   hydrolysis gives methyl alcohol and/or dimethyl ether.

A particularly useful class of solid, strongly
acidic catalysts are those derived from halides,
oxyhalides, oxides, sulfides and oxysulfides of metals,
15   particularly transition metals of Groups IV, V, VI, VIII
of the Periodic Table, such as of tantalum, niobium,
zirconium, tungsten, titanium, chromium and the like, or
mixtures thereof, deposited on suitable chalcide carriers,
such as alumina, zirconia or silica-alumina. These
20   catalysts are capable of effecting the ready conversion of
methane to methyl halides.

As noted in Olah, G.A. "Friedel-Crafts
Chemistry," N.Y., Wiley-Interscience, 1973. p. 343-344,
25   the elements of Group VIA such as oxygen, sulfur, selenium
or tellurium, have been called "chalcogens", and compounds
containing these elements are called "chalconites",
"chalcogenides" or "chalcides." A variety of solid oxides
and sulfides, especially those comprising alumina, silica
30   and mixtures of alumina and silica, either natural or
synthetic, in which other oxides such as chromia,
magnesia, molybdena, thoria, tungstic oxide, zirconia,
etc., may also be present, as well as sulfides of
molybdenum are useful chalcide carriers. Many naturally
35   occurring compositions exist for use as the carriers

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including: bauxite, floridin, Georgia clay, and other natural aluminosilicates.

Synthetic chalcides, other than those of the
5 silica-alumina type, representative of the chalcide carriers are: BeO, Cr_2O_3, P_2O_5, ThO_2, TiO_2, $Al_2(SO_4)_3$ (which may be regarded as $Al_2O_3 \cdot 3SO_3$), $Al_2O_3 \cdot Cr_2O_3$, Al_2O_3, Fe_2O_3, $Al_2O_3 \cdot CoO$, $Al_2O_3 \cdot MnO$, $Al_2O_3 \cdot V_2O_3$, $Al_2O_3 \cdot Mo_2O_3$, $Cr_2O_3 \cdot Fe_2O_3$,
10 MoS_2, and MoS_3.

The acidic chalcide supports are physically and chemically stable. They are generally catalytically active at only higher temperatures, as their acidity is
15 not great enough to lead them to form stable complexes with unsaturated compounds, as do the aluminum halides, for example.

Another class of useful solid strongly acidic
20 catalysts are the strong Bronsted or conjugated Lewis-Bronsted superacid catalysts. These catalysts include Bronsted-type perfluorinated sulfonic acids of 4 to 18 carbon atoms deposited on a suitable inert carrier or polymeric resin-sulfonic acid catalysts. These solid
25 superacid catalysts have a Hammett acidity function (H_o) of less than -11.9, the value for 100 percent sulfuric acid.

The supported Group VIII metal catalysts include
30 the various Group VIII metals supported on suitable chalcide carriers. Particularly useful are platinum and palladium supported on alumina, silica, active carbon, barium sulfate or related carriers.

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The Process Conditions

It is my invention that a practical process has
been found for the selective acidic or metal catalyzed
5   halogenation of methane to methyl monohalides (chloride,
bromide, iodide or fluoride).

The acidic halogenations are carried out over
solid acidic catalysts, particularly supported metal-based
10 catalysts, preferably selected from transition metal
halides, oxides or oxyhalides, such as those of iron,
tantalum, niobium or zirconium, on alumina, baria, or
other neutral oxides, barium sulfate or related carriers,
or over solid Bronsted-type perfluorinated sulfonic acids
15 of 4 to 18 carbon atoms deposited on a suitable inert
carrier or polymeric resinsulfonic acid catalysts at
temperatures between about 100 to 500°C, preferably
between 200 and 325°C.

20   Metal catalyzed reactions are carried out over
supported metal catalysts, preferably of the Group VIII
metals, on alumina, baria, or other neutral oxides, barium
sulfate or related carriers, at temperatures between 100
and 350°C, preferably between 200-300°C.
25

The solid acidic reactions are considered to take
place via surface catalytic activation of chlorine,
bromine, or iodine to an electrophilic halogen species.
The selective nature of the reactions is reflected by the
30 fact that even when using an excess of halogen (methane to
chlorine ratio of 1:2 to as high as 1:8), methyl halides
are formed in 85 to $>$99% selectivity over methylene
halides.

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At the same time, highly selective (99%) monochlorination is readily achieved when reacting excess methane (methane to chlorine ratio from 1:1 to 8:1) over the same catalysts. Excess methane under these conditions
5 is also a diluent for the system and eliminates any potentially explosive mixtures.

It is a further part of my invention that similar selective monohalogenation of methane was also discovered
10 to be possible using supported metal catalysts on alumina, baria, or other neutral oxides, barium sulfate or related carriers. In these reactions, an intermediate insertion of the metal in a C-H bond is premised with subsequent chlorinolysis.
15

In a similar fashion bromination and iodination of methane can also be achieved both in acid catalyzed electrophilic and metal promoted halogenations.

20 Fluorination of methane is also possible, but necessitates high dilution, preferably with an inert gas, and handling difficulties associated with the use of elemental fluorine. When the halogenation of methane is carried out in a fashion that the halogenation step is
25 directly followed, without separation of products, by passing the mixture together with anhydrous hydrogen fluoride, over a catalyst such as fluoridated alumina or higher valency metal fluorides, such as cobalt trifluoride, antimony perfluoride, or the like transition
30 metal fluorides, methyl fluoride is formed directly from methane without the use of elemental fluorine.

Hydrogen chloride, bromide and iodide by-products of the reactions can be readily recycled via
35 oxyhalogenation and thus reused.

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Methyl halides formed in the selective
halogenations disclosed in my invention can be used,
according to my co-pending application Serial No. 290,292
in the production of lower olefins and hydrocarbons of the
5   gasoline range, when treated over bifunctional
acidic-basic catalysts.

The methyl halides readily obtainable in high
yield and selectivity according to my invention are also
10 conveniently used via their hydrolysis either under
thermal or catalytic conditions, to produce methyl alcohol
and/or dimethyl ether. The conversion of methane to
methyl alcohol can be accordingly carried out as a
two-step process, but also can be practiced as a
15 single-step process converting methane directly to methyl
alcohol (and/or dimethyl ether) when reacting methane in
the presence of water (steam) with halogens. In this
application, acidic oxides, oxyhalides or Bronsted acidic
catalysts, compatible with water, are preferred.
20

$$CH_4 \xrightarrow[\text{H}_2\text{O}]{\text{X2}} CH_3OH + 2XCl$$
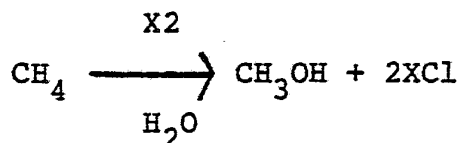
25 As hydrogen halides (X = Cl, Br, I) can be readily
recycled via oxyhalogenation, the disclosed process
represents a viable and energy saving alternative to the
production of methyl alcohol from CO and H_2, i.e.,
syn-gas.
30

In all of the reactions discussed, the catalyst
is preferably present in an amount of 0.1 to 25% based on
the amount of methane.

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The following examples are illustrative and are set forth for the purpose of illustration only and are not to be construed as limiting the scope of the invention in any manner. In the related Tables, the product compositions have been normalized, even if not stated, to provide 100 percent conversion, excluding unreacted methane which can be recycled.

Example 1

A mixture of methane and chlorine in the molar ratios indicated, was reacted over a 20% tantalum oxyfluoride catalyst deposited on alumina in a continuous flow reactor at 235°C to 300°C, respectively. The conversions per pass and product compositions were as follows:

Reaction Temp. °C	235	235	300	240	240	240
$CH_4:Cl_2$ ratio	1:2	1:4	1:2	2:1	4:1	8:1
% Conversion	13*	88*	40*	91**	95**	99**

* based on methane
** based on chlorine

% Product composition

methyl chloride	75	96.5	90	99	99	99
methylene chloride	-	trace	10	trace	trace	trace
ethane	25	-	trace	-	-	-
ethyl chloride	-	3.5	-	-	-	-

Example 2

Methane and chlorine in a molar ratio of 1:2 were passed at 250°C over a 20% niobium oxyfluoride catalyst

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supported on alumina. The product composition obtained
with 39% conversion was the following:

% Product composition	
methyl chloride	98
methylene chloride	2

5

Example 3

10   Methane and chlorine in a molar ratio of 1:4 were
passed over a 20% zirconium oxyfluoride catalyst on
alumina in a continuous flow reactor at 270°C. With 30%
conversion per pass the following product composition was
obtained:

15

%·Product·composition	
methyl chloride	96.5
methylene chloride	3.5

20 Example 4

          A mixture of methane and chlorine in a molar
ratio of 1:4 was reacted over a 20% antimony oxyfluoride
catalyst deposited on alumina at 250°C. A 19% conversion
25 per pass gave the following product composition:

% Product composition	
methyl chloride	86
methylene chloride	5
ethyl chloride	9

30

Example 5

35   A 1:4 molar mixture of methane and chlorine was
reacted over a Nafion-H perfluorinated polymeric

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resinsulfonic acid catalyst at 185°C, giving a 16%
conversion and the following product composition:

% Product composition

methyl chloride	93
methylene chloride	1
ethyl chloride	6

Example 6

A 1:2 molar mixture of methane and bromine was
reacted in the presence of a 20% antimony oxyfluoride
catalyst supported on alumina at 200°C. With a 36%
conversion per pass, the following product composition was
obtained:

% Product composition

methyl bromide .	87
ethylene bromide	3
ethyl bromide	0.5
butanes	9.5

Example 7

A 1:3 molar mixture of methane and chlorine was
passed at 250°C over a 1% iron catalyst supported on
alumina with a 59% conversion per pass. The following
product composition was obtained:

% Product composition

methyl chloride	97
ethyl chloride	3

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Example 8

     Methane and chlorine were passed over a 0.5%
platinum catalyst deposited on alumina. The conversions
and product composition obtained were the following:

Reaction Temp. °C	200	200	250	250
$CH_4:Cl_2$ ratio	1:2	1:1	2:1	4:1
% Conversion	50*	44*	74**	82**

* based on methane
** based on chlorine

% Product composition

methyl chloride	92	99	99	99
methylene chloride	8	trace	trace	trace

Example 9

     Methane and chlorine were passed at 200°C over a
0.5 palladium catalyst deposited on barium sulfate. The
conversions and product composition obtained were the
following:

Reaction Temp. °C	200	200
$CH_4:Cl_2$ ratio	1:2*	2:1**
% Conversion	29	69

* based on methane
** based on chlorine

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% ·Product composition

methyl chloride	99	99
ethylene chloride	trace	trace

Example 10

A 1:1:1 molar mixture of methane, bromine and water was reacted over a 20% tantalum oxyfluoride catalyst supported on alumina at 260°C. With a 77% conversion, the following product compositon was obtained:

methyl bromide	64%
methyl alcohol + dimethyl ether	31%
ethyl bromide	3%
$C_3 + C_4$	2%

Example 11

A 1:1:1 molar mixture of methane, chlorine and water was reacted over a 20% tungsten oxide on alumina catalyst at 250°C. With a 49% conversion, the following product distribution was obtained.

methyl chloride	68%
methyl alcohol + dimethyl ether	24%
ethyl chloride	6%
methylene chloride	trace
$C_3 + C_4$	2%

Example 12

A 1:5 molar mixture of methyl chloride and steam was passed, in a continuous flow reactor, over a catalyst

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composed of 10% zinc oxide on alumina containing 10%
aluminum hydroxide at 385°C. A 29% conversion per pass of
methyl alcohol was obtained with 98% selectivity.

5 Example 13

Under conditions of Example 12, when carrying out
the reaction with a catalyst composed of 10% magnesium
oxide on alumina containing 10% aluminum hydroxide at
10 420°C, a 21% conversion to methyl alcohol was obtained
with 98% selectivity.

Example 14

15 Under conditions of Example 12, when carrying out
the reaction with a catalyst composed of 10% titanium
oxide on alumina containing 10% aluminum hydroxide, a 18%
conversion to methyl alcohol was obtained with 98%
selectivity.

20 .

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Claims

I Claim:

5   1.   A process for the selective catalytic
production of methyl monohalides from methane carried out
at temperatures between about 100 and 500°C in the
presence of a halogen using as the catalyst a solid
strongly acidic catalyst.

10   2.   The process of claim 1 utilizing an acidic
supported catalyst selected from the Group IV, V, or VI
transition metal oxides or oxyhalides, supported on a
chalconite carrier.

15   3.   The process of claim 2 wherein the transition
metal is tantalum, niobium, zirconium or titanium and the
chalconite carrier is alumina.

20   4.   The process of claim 1 utilizing a strong
Bronsted acid catalyst selected from a perfluorinated
sulfonic acid of 4 to 18 carbon atoms deposited on an
inert carrier or perfluorinated polymeric sulfonic acid
resin.

25   5.   A process for producing methyl alcohol and/or
dimethyl ether by hydrolysis of methyl halides obtained by
one of claims 2 or 3, by treatment thereof in the presence
of water with an acidic oxide or oxyhalide catalyst.

30   6.   A process for the selective catalytic
production of methyl monohalides from methane carried out
at temperatures between about 100 to 300°C in the presence
of a halogen using as the catalyst a supported Group VIII
35 metal catalyst.

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7. The process of claim 6 utilizing a Group VIII
metal supported on alumina, silica, active carbon, barium
sulfate or other carriers.

5

8. The process of one of claims 1 or 6 wherein
the catalyst is present in amounts of 0.1 to 25% by weight
based on the amount of methane feed.

INTERNATIONAL SEARCH REPORT

International Application No `PCT/US82/01099`

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC³ C07C 29/00; C07C 41/01; C07C 17/10
U.S. Cl. 568/671; 568/891; 570/123; 570/161; 570/168; 570/253-255

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
U.S.	568/891, 893, 671 570/123, 161, 168, 253-255

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 2,156,039, Published 25 April 1939, DACHLAUER ET AL	1,4,6-8
X	US, A, 1,723,442, Published 06 August 1929, ROKA	1,4,6-8
X	US, A, 1,591,984, Published 13 July 1926, KRAUSE ET AL	1,4,6-8
X	US, A, 1,688,726, Published 23 October 1928, McKEE	5
X	US, A, 3,172,915, Published 09 March 1965, BORKOWSKI ET AL	5
X	US, A, 3,562,321, Published 09 February 1971, BORKOWSKI ET AL	5
X	US, A, 1,086,381, Published 10 February 1914, MASLAND	5
X	SU, A, 388529, Published 05 April 1976, ENGLIN	1
X	GB, A, 1017152, Published 19 January 1966, VECCHIO	2-4
X	GB, A, 1104294, Published 21 February 1968, KUY	5
X	OLAH, FRIEDEL-CRAFTS AND RELATED REACTIONS, INTERSCIENCE PUBLISHERS, NEW YORK, 1963, page 26	4
X	NAFION PAMPHLET, DUPONT, April 1978 "PERFLUOROSULFONIC ACID PRODUCTS"	4

* Special categories of cited documents: ¹⁵

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"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²
12 October 1982	21 OCT 1982

International Searching Authority ¹	Signature of Authorized Officer ¹⁹
ISA/US	Howard T Mars

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