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CATALYSTS FOR THE PRODUCTION OF
METHANOL AND OTHER CARBON COM-
POUNDS

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10 Claims. (Cl. 23—237)

This invention relates to chemical reactions in
the gaseous phase and particularly to the produc-
tion of oxygenated hydrocarbons by catalysis
from gaseous mixtures. The present application
is a division of my copending application Serial
Number 202,165, filed June 28, 1927.

It is known that oxygenated hydrocarbons, and
particularly methanol and its homologues, may
be prepared synthetically by passing a gaseous
mixture containing carbon monoxide and hydro-
gen under pressure over a catalyst. The syn-
thesis depends upon reactions of which the fol-
lowing for methanol is characteristic:



In my copending application Serial No. 183,905
I have described a process for manufacturing
oxygenated hydrocarbons and especially me-
thanol, the process involving the use of catalysts
prepared by fusing and subsequently reducing a
mixture of copper oxide and manganese oxide.

It is the object of the present invention to pro-
vide a further improvement in the process de-
scribed in the aforementioned copending ap-
plication.

Other objects and advantages will be apparent
as the invention is better understood by refer-
ence to the following specification in which its
preferred embodiments are described.

I have discovered that improved results may
be obtained in carrying out reactions in the gase-
ous phase in the presence of a catalyst consisting
of a reduction product of a fused mixture of
copper oxide and manganese oxide, if there is
incorporated in said catalyst one or more of the
elements magnesium, aluminum, chromium, zir-
conium, vanadium, titanium, thorium, silicon and
cerium.

The catalysts herein described exhibit an activ-
ity superior to that of a catalyst consisting of
fused and reduced copper oxide and manganese
oxide alone; and also superior to that of any of
the foregoing list of elements taken singly or in
combination with each other. The term "super-
ior activity" is used to indicate that with a given
rate of gas flow the catalysts give a higher yield
of product per hour or, correspondingly, to at-
tain a given hourly production a lower rate of gas
flow may be maintained.

In carrying out the invention the prepared
catalyst is disposed in a suitable receptacle adapt-
ed to withstand the pressure at which the reac-
tion is conducted. The gaseous mixture is in-
troduced at the proper temperature which may be
regulated and maintained in any desired way.

The gaseous mixture containing the product of
the reaction is withdrawn and cooled to effect
condensation of the product or is treated other-
wise for the recovery thereof.

The catalysts are particularly well adapted for
the synthesis of methanol from gaseous mixtures
containing hydrogen and carbon monoxide. This
reaction may be conducted with the described
catalysts at various pressures and temperatures,
but I prefer to carry out the synthesis of me-
thanol at a pressure within the range of 400 to
1000 atmospheres and at a temperature of 250°
to 500° C. The usefulness of the catalysts is not
limited to the treatment of gaseous mixtures of
any particular composition, it being possible to
effect the synthesis of methanol, for example,
with the improved catalysts by introducing gase-
ous mixtures containing hydrogen and carbon
monoxide in which the proportion of the latter
is relatively low, for example, between 3 and
15%. If the gaseous mixtures contain relatively
higher proportions of carbon monoxide the reac-
tion proceeds more vigorously, greater quantities
of heat are evolved and corresponding provision
must be made, therefore, for the dissipation of
heat so that the catalyst may not be damaged by
overheating and undesirable side reactions, such
as methanation, may be avoided.

The following examples will serve to indicate
the preferred procedure in preparing and utiliz-
ing catalysts such as are described herein, it be-
ing understood, however, that the invention is
not limited to the details of operation or the
particular conditions as set forth.

Example 1.—Prepare an intimate mixture of
seventy-five parts by weights of pure cupric
oxide, twenty parts of pure manganese dioxide
and five parts of pure magnesium oxide. The
mixture is fused, allowed to cool and crushed to
suitable size. The crushed material is then re-
duced slowly at 150° to 350° C. and at atmospheric
pressure in a current of pure hydrogen. Since
the reduction process is exothermic it should be
carried out slowly and with care so that the
catalyst may not be damaged by excessive tem-
perature. The catalyst thus prepared may be
employed for the production of methanol by pass-
ing a gaseous mixture containing hydrogen and
carbon monoxide in the volume ratio of twenty
to one at a space velocity of 100,000 to 150,000, a
pressure of 900 atmospheres and while main-
taining a temperature within the range of 250° to
400° C. The principal product is methanol, which
is associated with some of its higher homologues.

The following examples indicate the preferred

proportions for preparing other catalysts included within the scope of the invention. These may be prepared and employed in the synthesis of methanol under the same conditions as are set forth in Example 1.

Example 2.—Eighty parts of pure cupric oxide, fifteen parts of pure manganese dioxide and five parts of pure chromic oxide.

Example 3.—Eighty-seven parts of pure cupric oxide, ten parts of pure manganese dioxide and three parts of pure aluminum oxide.

Example 4.—Eighty-two parts of pure cupric oxide, fifteen parts of pure manganese dioxide and three parts of pure zirconium oxide.

Example 5.—Eighty-five parts of pure cupric oxide, ten parts of pure manganese dioxide and five parts of pure vanadium oxide.

Example 6.—Eighty-seven parts of pure cupric oxide, ten parts of pure manganese dioxide and three parts pure titanium oxide.

Example 7.—Seventy-eight parts of pure cupric oxide, twenty parts of pure manganese dioxide and two parts of pure thorium oxide.

Example 8.—Seventy-five parts of pure cupric oxide, twenty parts of pure manganese dioxide and five parts of pure silica.

Example 9.—Seventy-nine parts of pure cupric oxide, twenty parts of pure manganese dioxide and one part of pure cerium oxide.

The catalysts described may be used in the synthesis of methanol and other oxygenated hydrocarbons and for conducting other reactions in the gaseous phase in a similar manner under conditions of pressure and temperature that may vary within a wide range, depending upon the particular nature of the desired reaction and of the product to be prepared. A catalyst containing two or more of the elements mentioned in combination with copper and manganese can be prepared similarly by combining the oxides of these elements. Such catalysts have the desirable characteristics hereinbefore mentioned and may be utilized in effecting various reactions in the gaseous phase including the production of oxygenated hydrocarbons such as methanol.

It is to be understood that while the gaseous mixtures employed need not be limited to those containing hydrogen and carbon monoxide exclusively, the gases should, nevertheless, be freed from impurities which are likely to deleteriously affect the catalyst, and of these the compounds of sulphur are the most commonly encountered. The sulphur compounds may be removed preliminarily from the gases by suitable treatment thereof in accordance with the well understood practice. In synthesizing methanol and the like, it is recommended that suitable precautions be taken for avoiding the presence of metals of the iron group (iron, nickel and cobalt) in the catalyst and in the gases that are to react.

I have no theory or explanation to offer for any changes which may occur in the composition of the catalysts during either their reduction or actual use. It may be that in some cases the reduction yields a lower and especially active oxide which in conjunction with the activated copper with which it is associated forms a mass peculiarly adapted for the catalytic production of oxygenated hydrocarbons. In any event, it is to be understood that the term catalyst as employed in the claims includes the contact mass in the form in which it may occur during its use.

It will be apparent from the foregoing that by providing new catalysts of superior activity and improved physical form, decreasing catalyst con-

sumption and improving smoothness of operation, and by thus facilitating the production of oxygenated hydrocarbons and other desirable products of synthetic and other reactions, the present invention represents a distinct advance in the art. While the invention has been described more particularly with reference to the synthesis of methanol, the improved catalysts and the process may be utilized with similar advantages in conducting other reactions in the gaseous phase.

The various details of apparatus and procedure may be modified to meet the particular conditions of the reaction, the products being recovered in any suitable or desirable way, it being possible in the synthesis of methanol, for example, at pressures above 200 atmospheres to practically completely condense methanol from the gases by cooling with water at ordinary temperature. The methanol can be separated otherwise and other products can be treated in the manner best adapted to effect the separation thereof in an economical and satisfactory way.

Various changes may be made in the details of operation hereinbefore described without departing from the invention or sacrificing any of the advantages thereof.

I claim:

1. The improved catalyst for reactions in the gaseous phase, comprising the reduction product of a fused mixture of copper oxide, manganese oxide and an oxide of one of the elements of the group magnesium, aluminum, and silicon.

2. The improved catalyst for reactions in the gaseous phase, comprising the reduction product of a fused mixture of copper oxide, manganese oxide and magnesium oxide.

3. The method of forming an improved catalyst for reactions in the gaseous phase, which comprises fusing a mixture of copper oxide, manganese oxide and an oxide of one of the elements of the group magnesium, aluminum, and silicon, cooling and crushing the fused mass and subjecting it to the action of a reducing agent at a temperature favorable to the reduction of the copper oxide.

4. The method of forming an improved catalyst for reactions in the gaseous phase, which comprises fusing a mixture of copper oxide, manganese oxide and magnesium oxide, cooling and crushing the fused mass and subjecting it to the action of a reducing agent at a temperature favorable to the reduction of the copper oxide.

5. An improved catalyst for reactions in the gaseous phase, comprising the reduction product of an intimate and substantially homogeneous mixture of copper oxide, manganese oxide, and an oxide of one of the elements of the group magnesium, aluminum, and silicon.

6. An improved catalyst for reactions in the gaseous phase, comprising the reduction product of an intimate and substantially homogeneous mixture of copper oxide, manganese oxide, and magnesium oxide.

7. An improved catalyst for reactions in the gaseous phase, comprising an oxide of a metal which is a member of the group consisting of magnesium, aluminum, and silicon, together with an oxide of manganese, intimately associated with copper, said catalyst being obtained by fusing together a mixture of oxides of the aforementioned elements, and reducing the resulting mixture, suitably solidified and subdivided.

8. An improved catalyst for reactions in the gaseous phase, comprising the reduction product

of a fused mixture of copper oxide, manganese oxide, and an oxide of one of the elements of the group magnesium, aluminum, and silicon, and obtained by reducing the solidified and subdivided mixture at a temperature between about 250-350° C.

9. An improved catalyst for reactions in the gaseous phase comprising copper, manganese oxide, and magnesium oxide, said catalyst being obtained by fusing together a mixture of cop-

per oxide, manganese oxide, and magnesium oxide and reducing the resulting mixture, suitably solidified and subdivided.

10. An improved catalyst for reactions in the gaseous phase comprising the reduction product of a fused mixture of copper oxide, manganese oxide, and magnesium oxide, and obtained by reducing the solidified and subdivided mixture at a temperature between about 250-350° C.

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