[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

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Improvements in or relating to the Manufacture of Oxygenated Organic Compounds.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 28, Hanover Square, London, W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements in organic syntheses and in particular in the production of oxygenated organic compounds.

I have found that oxygenated organic compounds may be produced by bringing methane to reaction with steam.

The gases or vapours are most advantageously brought to reaction in presence of catalytic agents, and in particular catalytic agents consisting of or containing metals, metal oxides or other metallic compounds. The reaction may be, and preferably is, conducted under pressure, for example 50 or 100 atmospheres or more, and is most advantageously effected at relatively high pressures, such as 200, 300 or 500 atmospheres or more. Again the reaction temperature may vary from relatively low temperatures such as 200° to relatively high temperatures such as 700° or more. Particularly valuable products are obtainable by using temperatures intermediate within this range, for example temperatures of 250°, 300°, 350°, 400° or 500° C.

A very large number of metals and metallic compounds have a catalytic effect upon the reaction. The alkaline earth metals may be used as catalysts or any of the metals of groups 4, 5, 6, 7 and 8 of the periodic system, and also in addition aluminium, magnesium and zinc. The alkali metals and their compounds are preferably used in conjunction with other metals. Copper, silver and gold have also a catalytic effect but as with the alkali metal compounds they are preferably used in conjunction with other metals or metal compounds. As examples of metallic catalysts which I may use for promoting the production of oxygenated organic compounds according to the present invention I may instance zinc, magnesium, calcium, aluminium, chromium, manganese, vanadium, molybdenum, titanium, iron, nickel and cobalt and the rare earth metals. Such metals may be used in the metallic state but are preferably used in the form of oxides or hydroxides or other compounds and particularly compounds with the metalloids, such as sulphur or arsenic, or as salts of the oxy acids of metalloids, for example phosphates, silicates and borates. It is frequently of advantage to use two or more of the above metals or their compounds in admixture or in chemical combination, and in this connection it may be stated that the various admixtures and chemical compounds containing two or more metals which influence favourably the production of oxygenated organic compounds from carbon monoxide or carbon dioxide and hydrogen are also of value in promoting or directing the reactions according to the present invention. As instances of such mixtures for use according to the present invention I may mention zinc chromate, manganese chromate, zinc vanadate, zinc manganate, zinc tungstate or zinc molybdate, or the corresponding salts of other metals such as magnesium, calcium or aluminium. I may also use any of the catalysts or catalyst mixtures containing cobalt, nickel and iron referred to in my copending applications Nos. 22,779/29 (Serial No. 337,014) and 22,780/29 (Serial No. 337,409). The relative proportions of metals in the particular catalyst mixture employed also exercises a directive influence on the course of the syntheses. For example alkali and alkali earth metals may be used in conjunction with other metals in any proportion but most valuable results are in general obtainable by employing equimolecular proportions or proportions in which the alkali or alkaline earth metal predominates, e.g. proportions of 1½ or 2 or more molecules of alkali or alkaline earth metal to 1 molecule of other metal.

For the purposes of the invention the methane may be used in conjunction with steam or in conjunction with steam and carbon monoxide or dioxide. To the reaction gases I may further add other gases capable of exercising either a reducing or oxidising effect. For example additions of oxygen may be made, such

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additions being preferably small in comparison with the total volume of the reaction gases, so as to produce compounds of a higher order of oxidation, such as aldehydes, ketones or acids. On the other hand additions of hydrogen may be made to the reaction gases so as to improve the yield of oxygenated organic compounds of a lower order of oxidation such as alcohols. The addition of inert gases such as nitrogen, to the reacting gases frequently tends to retard the production of undesirable gaseous decomposition products.

The reaction according to the present invention may be conducted in any suitable apparatus, for example apparatus made of copper or alloys of copper, or of steel lined with copper or alloys of copper, or made of steel containing vanadium, manganese, cobalt, nickel or the like.

Dated this 24th day of July, 1929.

WHITEHEAD & STEPHENS,
Chartered Patent Agents,
Celanese House,
22 & 23, Hanover Square, London, W.1.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Oxygenated Organic Compounds.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, W.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of oxygenated organic compounds from methane by the subjection of methane to the action of steam.

According to the invention I have found that oxygenated organic compounds can be produced from methane in a highly satisfactory manner by subjecting methane to the action of steam at temperatures between 200° and 500° C.

For performing the invention the gases or vapours are most advantageously brought to reaction in presence of catalytic agents, and in particular catalytic agents consisting of or containing metals, metal oxides or other metallic compounds. The reaction may be, and preferably is, conducted under pressure, for example 50 or 100 atmospheres or more, and is most advantageously effected at relatively high pressures, such as 200, 300 or 500 atmospheres or more.

A very large number of metals and metallic compounds have a catalytic effect upon the reaction. The alkaline earth metals may be used as catalysts or any of the metals of groups 4, 5, 6, 7 and 8 of the Periodic System, and also in addition aluminium, magnesium and zinc. The alkali metals and their compounds are preferably used in conjunction with other metals. Copper, silver and gold have also a catalytic effect but as with the alkali metal compounds they are preferably used in conjunction with other metals or metal compounds. As examples of metallic catalysts which I may use for promoting the production of oxygenated organic compounds according to the present invention I may instance zinc, magnesium, calcium, aluminium, chromium, manganese, vanadium, molybdenum, titanium, iron, nickel and cobalt and the rare earth metals. Such metals may be used in the metallic state but are preferably used in the form of oxides or hydroxides or other compounds and particularly compounds with the metalloids, such as sulphur or arsenic, or as salts of the oxy acids of metalloids, for example phosphates, silicates and borates. It is frequently of advantage to use two or more of the above metals or their compounds in admixture or in chemical combination, and in this connection it may be stated that the various admixtures and chemical compounds containing two or more metals which influence favourably the production of oxygenated organic compounds from carbon monoxide or carbon dioxide and hydrogen are also of value in promoting or directing the reactions according to the present invention. As instances of such mixtures for use according to the present invention I may mention zinc chromate, manganese chromate, zinc vanadate, zinc manganate, zinc tungstate or zinc molybdate, or the corresponding salts of other metals such as magnesium, calcium or aluminium. I may also use any of the catalysts or catalyst mixtures containing cobalt, nickel and iron referred to in my co-pending Application No. 22,779/29 (Serial No. 337,014), namely catalysts consisting of or comprising one or more

ferrites, ferrates, cobaltites, cobaltates and particularly ferrites, ferrates, cobaltites or cobaltates of the alkali or earth alkali metals, or in my co-pending Application No. 22,780/29 (Serial No. 337,409), namely catalysts comprising iron, nickel or cobalt in the form of their borates, silicates, phosphates or salts of other oxy-acids of phosphorus. The relative proportions of metals in the particular catalyst mixture employed also exercise a directive influence on the course of the syntheses. For example alkali and alkali earth metals may be used in conjunction with other metals in any proportion but most valuable results are in general obtainable by employing equimolecular proportions or proportions in which the alkali or alkaline earth metal predominates, e.g. proportions of 1½ or 2 or more molecules of alkali or alkaline earth metal to 1 molecule of other metal.

For the purposes of the invention the methane may be used in conjunction with steam or in conjunction with steam and a gas or gases capable of yielding oxygen. for instance carbon monoxide or dioxide. To the reaction gases I may further add other gases capable of exercising either a reducing or oxidising effect. For example additions of oxygen may be made such additions being preferably small in comparison with the total volume of the reaction gases, so as to produce compounds of a higher order of oxidation, such as aldehydes, ketones or acids. On the other hand additions of hydrogen may be made to the reaction gases so as to improve the yield of oxygenated organic compounds of a lower order of oxidation such as alcohols. The addition of inert gases, such as nitrogen, to the reacting gases frequently tends to retard the production of undesirable gaseous decomposition products.

The reaction according to the present invention may be conducted in any suitable apparatus, for example apparatus made of copper or alloys of copper, or of steel lined with copper or alloys of copper, or made of steel containing vanadium, manganese, cobalt, nickel or the like.

The following examples serve to illustrate convenient forms of execution of the invention, it being understood that they are given only by way of illustration and are in no way limitative.

EXAMPLE 1.

A mixture of steam and methane containing about 1—5 parts by volume of steam to each part of methane is passed under a pressure of about 180—250 atmospheres over or in contact with a catalyst mass composed of a mixture of potassium bichromate and zinc oxide (e.g. containing between 20 and 50% zinc oxide) heated to a temperature between 350° and 450° C.

There results a copious yield of oxygenated organic compounds composed essentially of ethanol and higher aliphatic alcohols, whilst the production of more oxidised products such as aldehydes, acids and ketones is substantially avoided.

EXAMPLE 2.

A mixture of steam, methane and oxygen containing about 1—5 parts by volume of steam to each part of methane and between 5 and 20% oxygen relatively to the steam, is passed under a pressure of between 150 and 250 atmospheres in contact with a catalyst mass composed of a mixture of zinc chromate and cobalt oxide (e.g. containing between 20 and 30% zinc chromate) at a temperature between about 380° and 500° C.

There results a copious yield of oxygenated organic compounds composed essentially of aliphatic aldehydes and acids (including acetic acid, acetaldehyde and higher acids and aldehydes) in substantial absence of aliphatic alcohols.

EXAMPLE 3.

A mixture of methane, steam and hydrogen containing between 1—5 parts of steam to each part of methane and containing between about 10 and 40% hydrogen relatively to the steam, is passed under a pressure of between about 150 and 200 atmospheres in contact with zinc chromate heated to a temperature of between 250° and 325° C.

There results a copious yield of oxygenated organic compounds composed substantially of methanol together with higher aliphatic alcohols.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. Process for the manufacture of oxygenated organic compounds from methane which comprises subjecting methane to the action of steam at a temperature between 200° and 500° C.

2. Process according to claim 1 and wherein the reaction is performed in presence of catalysts consisting of or comprising metals, metal oxides or other metal compounds.

3. Process according to claim 1 and wherein the reaction is performed in presence of one or more of the following metals, and particularly in presence of one or more of the following metals in the form of their oxides, hydroxides, or other compounds, namely:—alkaline earth metals, metals of groups 4, 5, 6, 7 and 8 of the Periodic System,

aluminium, magnesium and zinc.

4. Process according to claim 1, 2 or 3 and wherein the reaction is performed under pressure and especially under pressures of between 50 and 100 atmospheres or more.

5. Process according to claim 1, 2, 3 or 4 comprising subjecting a mixture of methane and steam and containing carbon monoxide or carbon dioxide to the reaction.

6. Process according to claim 1, 2, 3, 4 or 5 comprising subjecting a mixture of methane and steam containing oxygen to the reaction.

7. Process according to claim 1, 2, 3, 4, 5, or 6 comprising subjecting a mixture of methane and steam containing a reducing gas, especially hydrogen, to the reaction.

8. Process according to any of the preceding claims and wherein the reaction mixture is diluted with an indifferent gas such as nitrogen.

9. Process for the manufacture of oxygenated organic compounds substantially as described in Example 1, 2 or 3.

10. Process for the manufacture of oxygenated organic compounds substantially as hereinbefore described.

11. Oxygenated organic compounds whenever prepared or produced by the process claimed in any of the preceding claims.

Dated this 15th day of May, 1930.

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