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(13) Patent:

(54) MANUFACTURING METHANOL SYNTHETICALLY
(54) PRODUCTION SYNTHETIQUE DE METHANOL

(72) Inventors (Country):

JOHANNES UFER (Not Available)
OTTO SCHMIDT (Not Available)

(73) Owner(s) (Country):

BADISCHE ANILIN AND SODA-FABRIK

(71) Applicant(s) (Country):

(74) Agent:

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Specification:

ALL WHOM IT MAY CONCERN:-

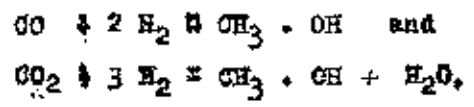
Be it known that we, Otto Schmidt and Johannes Ufer, Chemists, of Ludwigshafen-on-Rhine, Germany, having jointly invented a certain new and useful improvement in MANUFACTURING METHANOL SYNTHETICALLY, do hereby declare that the following is a full, clear and exact description of the same.

It has not been possible so far to produce methyl alcohol successfully by the catalytic reduction of carbon monoxid, though several proposals have been made to this effect.

We have now found that methanol can be produced by the catalytic reduction of carbon oxide with very good yields and a good speed of the reaction so that an industrial utilization of the process is rendered possible, by employing contact masses which contain, besides one or several catalytically acting elements, also titanium, vanadium, chromium or manganese or other elements of the fourth, fifth, sixth or seventh groups of the periodic system related to the aforementioned ones, or boron, or compounds of these elements, or more than one of these elements or compounds thereof. As instances of such other elements, cerium, thorium, uranium, molybdenum or tungsten may be mentioned, but other cognate elements of the said groups may also be employed.

It is of advantage to use gas mixtures of carbon monoxid or dioxide, or both and hydrogen with quantities of the latter exceeding by volume the quantities of the oxide of carbon and preferably, in the proportions calculated according to the formulae :

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or with even more hydrogen. Such exceeding quantities of hydrogen or hydrocarbons must be used when contact masses are employed consisting of mixtures of zinc with the oxide of chromium, manganese, molybdenum, titanium or cerium. A high excess of hydrogen may be present for example 1½ of the calculated volume or a multiple of the latter. The gas mixture may also contain nitrogen, hydrocarbons and the like, and it may be purified and dried,

prior to the reaction.

With the beforementioned conditions, a very pure methanol is obtained at comparatively low temperatures.

The contact masses may be prepared in any suitable way and the proportions of the components may be varied within wide limits. Inter alia, the additional elements mentioned may be compounded, in the form of their higher oxides with an acid character, with the catalytically acting elements to form a salt, and such salts, for instance vanadates, chromates, manganates, borates, may be subjected to reduction. Mixtures of such acids with the catalytic elements may also be used and the contact mass may be prepared in any other way. Supports may also be employed and most various substances may serve this purpose.

In order to produce a very pure methanol it has proved useful to employ catalysts of the aforesaid kind which contain as little alkali as possible and accordingly to purify thoroughly those contact masses which contain any alkali from their preparation prior to their use for the present process, or to exclude any alkali compounds when preparing the contact masses. When supports are employed, such materials should be used as do not give off any alkali. Thereby the formation of oily products is prevented or greatly diminished.

The temperatures of the reaction may be raised to above 500 degrees Centigrade, but in general they need not exceed 300 degrees Centigrade and in many cases considerably lower temperatures are sufficient which are in favor of the formation of pure methanol. The pressure may be raised to any degree. Less active contact masses require very high pressures and rather high temperatures in order to give ample yields.

In all cases it is important that iron or nickel is not present or only in comparatively small amounts and only together with other catalytically acting metals, as otherwise methane, or other hydrocarbons may be formed.

The process is further explained by the following examples, but we wish it to be understood that the invention is in no way restricted to these examples. The parts are by weight where no other statement is made.

Example 1.

Prepare a catalyst by introducing 50 parts of asbestos wool into a solution of 86 parts of copper nitrate and from 8 to 10 parts of chromium acetate, heat to boiling, precipitate with sodium carbonate, filter, wash well and dry. Then loosen the asbestos wool and reduce it at between 190 degrees to 200 degrees Centigrade by means of hydrogen. Over the contact mass thus prepared a gas mixture containing 20 parts, by volume, of hydrogen, for each one part of carbon monoxid is passed at a temperature of from 220 degrees to 250 degrees Centigrade and at a pressure of about 100 atmospheres. Methanol is formed with an excellent yield, besides small amounts of oily matter, insoluble in water, and a little methane may sometimes be formed.

Mixtures of carbon dioxide and hydrogen may also be employed which may contain carbon monoxid, nitrogen, hydrocarbons and other gases.

Example 2.

Introduce 50 parts of asbestos into a dilute solution of 56 parts of potassium dichromate then add 70 parts of copper nitrate whereby copper chromate is precipitated on the asbestos fibre. Then wash, dry, loosen the asbestos and reduce in an atmosphere of hydrogen at about 200 degrees Centigrade. With the aid of this contact mass, methanol is produced already at 220 degrees Centigrade with excellent yield. Very good yields are also obtained with the chromates of silver, or of silver and copper, or with the molybdates or tungstates of silver, or copper or other catalytically acting metals, or with other salts of mixtures including those with more than one catalytically acting metals or more than one additional element.

Example 3.

Dissolve in water 25 parts of neutral copper acetate and 21.3 parts of silver nitrate, then add 50 parts of asbestos wool, heat to boiling, add 25 parts of chromic acid, evaporate while mixing at intervals, dry, loosen the mass and reduce in a current of hydrogen at about 400 degrees Centigrade and 25 atmospheres. When a mixture of carbon monoxid and hydrogen (with about 1 volume of the former to each 6 volumes of the latter) is passed over this contact mass at

about 230 degrees Centigrade and 120 atmospheres, methanol is formed with good yield.

A contact mass prepared by decomposing potassium chromate with copper acetate and lead nitrate in the presence of asbestos wool can be employed in a similar manner.

Example 4.

84 parts of copper nitrate and 10 parts of uranium nitrate are dissolved in water and 50 parts of asbestos wool are introduced. The mixture is then heated to boiling, precipitated with caustic potash lye, filtered thoroughly, washed, dried and loosened. The mass produces methanol at 220 degrees Centigrade with very good yield and at great speed.

Example 5.

A mixture of carbon monoxid and hydrogen, in the proportions of about 1 to 10 is passed at about 260 degrees Centigrade and at a pressure of 100 atmospheres over a contact mass containing 63.6 parts of copper, 11.4 parts of uranium and 3.9 parts of manganese deposited as hydroxids or carbonates on a carrier. On cooling the reaction gas methanol condenses with an excellent yield. The percentage of either uranium or manganese or both may also be higher.

Example 6.

Pass a mixture of 10 parts, by volume, of carbon monoxid and 90 parts, by volume, of hydrogen at about 220 degrees Centigrade and a pressure of 100 atmospheres over a catalyst consisting of asbestos with an intimate mixture of 50 parts of manganese dioxid, 30 parts of copper oxid, 15 parts of cobalt oxid and 5 parts of silver oxid precipitated thereon which has been reduced beforehand at a temperature of about 200 degrees Centigrade in a current of hydrogen. The reaction gas leaving the catalyst will deposit, on cooling, a liquid chiefly consisting of methanol.

Very good results are also obtained when employing salts of the acid higher oxids of the elements of the fifth or seventh groups with catalytically acting elements. For example the reduction products of copper or silver vanadate, copper or silver manganate or the like may be used.

Example 7.

Dissolve so much of copper nitrate as corresponds to 21.8 parts of copper and 10 parts of thorium nitrate in water, add 50 parts of asbestos, heat to boiling, precipitate with an excess of caustic potash lye, filter off, wash thoroughly, dry, loosen the asbestos and reduce in a current of hydrogen at a temperature of about 200 degrees Centigrade.

When a dry mixture of carbon monoxid and hydrogen in the proportions of about 1 to 7 is passed over this mass at a temperature of about 220 degrees Centigrade and a pressure of 100 atmospheres, methanol is produced with good yield.

Example 8.

Dissolve so much of copper nitrate as corresponds to 21.8 parts of copper, 10 parts of uranyl nitrate and 5 parts of thorium nitrate in water, add 50 parts of asbestos wool, heat to boiling, precipitate with an excess of caustic potash lye, filter off, wash thoroughly, dry, loosen and reduce at a temperature of about 200 degrees Centigrade in a current of hydrogen. When a dried mixture of carbon monoxid and hydrogen in the proportions of about 1 to 5 is passed over this catalyst at a temperature of about 220 degrees Centigrade, reaction takes place at about 35 atmospheres and a liquid is obtained with good yields chiefly consisting of methanol. Other organic compounds especially oily substances are either not at all obtained or only in very small amounts.

If instead of a mixture of hydrogen and carbon monoxid, a mixture of hydrogen and carbon dioxide, for example in the proportion of 5 to 1, is passed over the said catalyst at a temperature of about 220 degrees Centigrade and a pressure of about 100 atmospheres the reaction gases on cooling, give off a liquid which is composed of water and chiefly methanol.

Example 9.

A contact mass is prepared from 21.8 parts of copper in form of the nitrate, 10 parts of uranyl nitrate, 5 parts of cerium nitrate and 50 parts of asbestos wool substantially as described in the foregoing

example, and a mixture of 1 volume of carbon monoxid and 10 parts of hydrogen is passed over this mass at a pressure of about 150 atmospheres or substantially less and at a temperature of about 220 degrees Centigrade. Methanol is recovered from the reaction gases by cooling.

The pressure and proportions of carbon monoxid or dioxid to hydrogen may be varied within a wide range, but the hydrogen should best be present in an exceeding quantity in all cases. The greater the pressure the greater the yield and the quantity of gases undergoing the reaction.

WHAT WE CLAIM AS OUR INVENTION IS:

1. The process of manufacturing methanol by the catalytic reduction of carbon monoxid, or dioxid, or both, with hydrogen and in the absence or presence of hydrocarbons or nitrogen which consists in passing the gas mixture at an elevated pressure and temperature over a catalyst containing one or more hydrogenating catalytic elements and one or more elements selected from the groups of titanium, vanadium, chromium and manganese and cognate elements, or boron, and removing methanol from the reaction gases preferably by cooling without releasing the pressure.
2. The within described process of manufacturing methanol, characterized by the employment of a gas mixture containing hydrogen in a volumetric proportion exceeding the volume of carbon monoxid, or dioxid, or both, and employing a pressure of at least 30 atmospheres and a temperature of 200 degrees Centigrade or higher.
3. The process of manufacturing methanol by the catalytic reduction of carbon monoxid, or dioxid, or both, with a greater volumetric proportion of hydrogen than of the carbon oxids at a pressure of at least 30 atmospheres and a temperature of about 200 degrees Centigrade or higher, which consists in passing the gas mixture over a catalytic mass containing one or more hydrogenating elements and one or more elements selected from the groups of titanium, vanadium, chromium and manganese and cognate elements, or boron, but free from iron and nickel.
4. The process of manufacturing methanol by the catalytic reduction of carbon monoxid, or dioxid, or both, with a greater volumetric proportion of hydrogen than of the carbon oxids, at a pressure of at least 30 atmospheres and a temperature of about 200 degrees Centigrade, or higher,

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which consists in passing the gas mixture over a catalytic mass containing copper and one or more elements selected from the groups of titanium, vanadium, chromium, and manganese and cognate elements, or boron, but free from iron and nickel.

5. The process of manufacturing methanol by the catalytic reduction of carbon monoxid, or dioxid, or both, with a greater volumetric proportion of hydrogen than of the oxide of carbon, at a pressure of at least 30 atmospheres and a temperature of about 200 degrees Centigrade, or higher, which consists in passing the gas mixture over a catalytic mass containing one or more hydrogenating elements and one or more elements selected from the groups of titanium, vanadium, chromium, and manganese and cognate elements, or boron, but free from iron and nickel and from alkali compounds, removing methanol from the reaction gases by cooling without releasing the pressure and conveying the residual gas again over a contact mass of the character aforescribed.

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