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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Process for the Production of Oxygen-containing Organic Compounds.

We, Société Chimique de la Grande-Paroisse Azote et Produits Chimiques, a Société Anonyme organised under the Laws of the French Republic, of 40, Rue du Colisée, Paris, France, 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 a process for the production of oxygen-containing organic compounds.

It has already been shown possible to produce formaldehyde on the one hand and formic acid on the other hand by the reaction of carbon monoxide and water in the liquid state or in the form of vapour in the presence of certain catalysts.

The present invention however provides a process for the production of oxygen-containing organic compounds of the lower (i.e. first six) members of the aliphatic series, which consists in causing carbon monoxide or carbon monoxide-containing gases and water in the state of liquid or vapour, to react in the presence of a single-phase catalyst comprising on the one hand, one of the elements, aluminium, silicon, cerium, titanium, zirconium and thorium, being elements included in the third or fourth groups, series *a*, of the periodic table and on the other hand, one of the elements, potassium, sodium, magnesium, chromium, molybdenum, manganese, copper, silver, zinc, cadmium, mercury, lead, arsenic, antimony, bismuth and vanadium, being elements not comprised in said groups and series set forth and not included in the iron group, under conditions of temperature and pressure precluding the formation of hydrogen as the main reaction product.

Term "single-phase catalyst", is intended to denote a catalyst which employs the combined and simultaneous action of a plurality of substances endowed with different catalytic properties.

The constituent elements of the catalyst may be employed in the free state or in the form of oxides, hydrates, or salts of organic or inorganic acids e.g. carbonates, formates, oxalates, borates, nitrates and phosphates.

The substances present in the single phase catalysts must however be stable in the conditions under which the process is carried out.

In the production of these single-phase catalysts the known methods for the preparation of this special class of catalyst are employed, such as simultaneous precipitation in a solvent, joint fusion and the like, every precaution being taken to ensure the utmost homogeneity.

These catalysts may, moreover, be produced or deposited on inert supports, or on highly porous substances, or on infusible or difficultly fusible substances, which increase their stability towards temperature by acting simply as diluents.

The catalyst whether prepared by simultaneous precipitation in a solvent, or by simple or oxidising fusion in a crucible or in an electric furnace or by alumino-thermic means, is treated before being used. The object of this treatment is to bring the catalyst into such a state of oxidation, hydration or combination that it will be stable under the conditions in which it is used. The treatment is generally performed in the apparatus in which the synthetic reaction takes place, and in such a manner as to prevent any further alteration of the catalyst through handling.

The catalysts used in carrying out the invention are progressively heated at ordinary pressure or under high pressure,—either in a current of the reaction gases or in hydrogen alone, or in carbon monoxide alone, or in steam, or in a current of carbon dioxide or nitrogen, or else in a current of one of the products of the desired reaction, such as the vapours of formic acid,—to a temperature which is lower than the temperature at which the catalysts are intended to be used, or in the neighbourhood thereof. By means of the above described single-phase catalysts it is possible to obtain, by the reaction of carbon monoxide with water, organic oxygen-containing compounds having various functions, such as alcohols, acids, ether salts and ether oxides,

[*Price* 1s.]

Price 4s 6d

Price 25p

ketones, aldehydes and the like. It should be understood that no general relation can be formulated between the relative quantitative composition of the substances produced by the reaction and the elementary composition of the catalysts. It will simply be stated that the introduction of strongly electro-negative elements into a catalyst, generally increases the production of substances of acid character.

The various syntheses are effected at different temperatures according to the pressure employed and the nature of the products to be obtained, and the conditions of temperature and pressure are so adjusted as to preclude the formation of hydrogen as the main reaction product. The temperatures lie between ordinary temperature and 550° C. and may for example be in the neighbourhood of 200—300° C. for aldehydes, 300—350° for acids, and 350°—450° C. for alcohols.

Some of these reactions, such as the syntheses of acids take place already at ordinary pressure. Others, such as the syntheses of alcohols, require a pressure of at least some tens of atmospheres. The most advantageous pressures lie between 50 and 600 atmospheres.

According to the temperature and pressure, the water is entirely or partially vaporised.

In carrying out the process use may be made of various known apparatus for the hydrogenation of oils.

The walls of the tubes or reaction vessels should be made, for example, of special chrome steels, or silicon steels or manganese steels, or they may be of copper, or silver, according to the nature of the product and the degree of purity desired.

All the usual precautions employed in the treatment of gas mixtures containing large proportions of carbon monoxide should be taken, such as the exclusion of iron, nickel and the like, from contact with the hot gases, the exclusion of iron carbonyl, nickel carbonyl and of the known poisons from the gases under treatment.

It should be noted that, on the other hand, the carbon monoxide employed may contain oxygen, hydrogen, carbon dioxide, nitrogen, methane and other saturated or unsaturated hydrocarbons which are not transformed or will simply furnish water, alcohols or ketones. On the other hand, there may be introduced into the reaction zone, simultaneously with the water, one or more products of the reaction, such as alcohols, acids and the like. This is particularly advantageous in cases where it is specially desired to obtain higher homologues of a similar nature to or different natures from those of the substances introduced.

The resulting products are condensed at ordinary temperature or retained by washing with water or solvents, or finally they may be liquefied or solidified by adequate cooling, the whole being advantageously effected under pressure.

The residual gases which generally contain hydrogen and nitrogen, in addition to carbon monoxide and carbon dioxide, may be employed again after suitable purification (for example elimination of the carbon dioxide) either by returning them to the cycle from which they are derived, or by passing them through another cycle, analogous with the first but furnishing other products as described in the present invention, or finally by passing them through other known cycles which utilise gases under pressure, such as the synthesis of ammonia or the synthesis of methyl alcohol according to the reaction $CO+2H_2=CH_3OH$.

EXAMPLE 1.

A solution of 9 grams of thorium oxide and 9 grams of potassium carbonate in formic acid is evaporated to dryness on pumice. A current of carbon monoxide under a pressure of 500 atmospheres is passed over this catalyst, and the temperature is gradually raised to 250° C. Thereupon a mixture of $3CO+H_2O$ is introduced at a space velocity of 2000 and a nearly normal solution of formic acid is collected whilst the residual gases contain only 1—2% of carbon dioxide.

EXAMPLE II.

A mixture of:—

10 grams Sb_2O_3 (antimonious oxide)
35 grams $Th(NO_2)_4$ (thorium nitrate)

is dissolved in concentrated hydrochloric acid. and parts with its nitric acid in the cold. The mixture is precipitated at boiling heat by means of ammonium carbonate, and the precipitate is kneaded, dried and broken to the size of a pea.

At 420° C., with an equi-molecular mixture of carbon monoxide and water under a pressure of 200 atmospheres with a space velocity of 1000, residual gases are obtained which contain 30% of carbon dioxide, (and 24% of carbon dioxide when the space velocity of 2000 is employed); whilst the resulting solution is heavier than water and contains alcohols and other organic oxygen compounds.

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

1). A process for the production of oxygen-containing organic compounds of the lower (i.e. first six) members of the aliphatic series, which consists in causing carbon monoxide or carbon monoxide-containing gases and water in the state of liquid or vapour, to react in the presence of a single-phase catalyst comprising on the one hand, one of the elements, aluminium, silicon, cerium, titanium, zirconium, and thorium, being elements included in the third or fourth groups, series *a*, of the periodic table and on the other hand, one of the elements, potassium, sodium, magnesium, chromium, molybdenum, manganese, copper, silver, zinc, cadmium, mercury, lead, arsenic, antimony, bismuth and vanadium, being elements not comprised in said groups, and series set forth and not included in the iron group, under conditions of temperature and pressure precluding the formation of hydrogen as the main reaction product.

2). A method of carrying out the process set forth in Claim 1, which consists in introducing into the reaction zone one or more of the reaction products.

3). The process for the production of oxygen-containing organic compounds substantially as described.

Dated this 17th day of April, 1928.

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Reference has been directed, in pursuance of Section 7, Sub-section 4, of the Patents and Designs Acts, 1907 to 1928, to Specifications Nos. 180,016 and 27,963 of 1913.

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