[Second Edition.]

PATENT SPECIFICATION

343,807

Convention Date (France): Feb. 7, 1930.

Application Date (in United Kingdom): April 10, 1930. No. 11,412 / 30.

Complete Accepted: Feb. 26, 1931.

3384

COMPLETE SPECIFICATION.

Process of Synthesising Organic Compounds Containing Oxygen.

We, Societe Chimique de la Grande-Paroisse Azote et Produits Chimiques, a Corporation 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 of synthesising organic compounds containing oxygen.

Various catalysts have already been described as capable of bringing about the reaction between carbon monoxide and water, with a view to the production of aliphatic organic compounds containing oxygen, such as alcohols, acid, ethers, aldehydes and ketones.

The present invention relates to a new series of such catalysts, which are characterised by the possession of properties of special advantage from the industrial point of view.

It is known, in fact, that, in addition to the specific part played by the components, the useful action of a catalyst is largely a function of its physical condition. The best results are obtained by means of catalytic masses containing a very large number of extremely fine pores.

On the other hand, from the industrial point of view, it is desirable that the cohesion and hardness of the grains of catalyst should be as high as possible.

This twofold result is obtained by composing the catalytic masses of substances with a zeolitic structure, that is to say, more or less analogous to the natural zeolites, or the artificial zeolites, such as that known under the Registered Trade Mark "Permutit".

It is known that these substances result from the union of salts of strongly alkaline character (alkali silicates, alkali borates and the like) with metallates (or salts of amphoteric metals), with or without addition of neutral, or substantially neutral, salts (metallic chlorides, sulphates, nitrates or acetates for example).

It is known that catalysts for the synthesis of organic compounds containing oxygen, can be prepared by associating at least one element of the series:

1). Potassium, sodium, lithium, vanadium, chromium, molybdenum, manganese, iron, cobalt, nickel, silver, copper, zinc, cadmium, lead, antimony, bismuth, calcium, strontium, barium, with at least one element of the series.

2). Beryllium, magnesium, aluminium, cerium, rare earths, boron, silicon, titanium, zirconium, thorium, uranium, tungsten.

Catalysts of a zeolitic nature can therefore be obtained by employing the above elements and by introducing them into the zeolite in a form suited to their particular chemical properties. In this connection it may be mentioned that the elements boron, silicon, titanium, zirconium, aluminium and beryllium, form strongly alkaline salts, that the elements vanadium, chromium, molybdenum, manganese, zinc, lead, antimony, uranium and tungsten are amphoteric, and finally that the elements potassium, sodium, lithium, manganese, calcium, barium, strontium, cerium, rare earths, iron, cobalt, nickel, cadmium, copper, silver, bismuth, and thorium, form salts which are appreciably neutral.

The introduction of the active catalytic elements may be effected in various ways:

1). All the necessary elements may be introduced into the catalyst as neutral salts, the remainder of the zeolite being composed of alkaline salts. For example, the first constituent may consist of sodium silicate, potassium silicate, borax and the like, with sodium aluminate, potassium aluminate, or other metallates, as the second constituent, and the mixture of the neutral salts of the catalytic elements as the third constituent.

2). One or more catalytic elements of amphoteric character may be introduced in the form of metallates, the sodium silicate or borax being retained as first constituent, and the other active elements added in the form of neutral salts.

3). One or more active elements of acid character may be introduced, in the form of alkaline salts, as the first constituent, and the other active elements in the form

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of metallates, or neutral salts.

4). Finally, the active elements of alkaline character may be introduced, in the form of silicates, borates and the like, into the first constituent, and the other active elements in the form of metallates or neutral salts.

In each particular instance, the method of introduction should be chosen which corresponds to the various properties of the constituent elements of the catalyst.

It should be noted, in general, that the introduction of an element into the matrix of the zeolite, or in a non-exchangeable form, increases the stability, but weakens the action of this element.

On the contrary, the elements introduced in the form of neutral salts are the most active, but the most unstable.

This remark, however, does not apply to the case in which the zeolitic catalysts are first put through a preliminary treatment of reduction, dehydration or transformation. In this particular case the chemical constitution of the zeolites often undergoes considerable modification, although its physical structure is retained and all the methods of introduction seem to be approximately equivalent.

The zeolites constituted in this manner can be prepared either by fusion or by precipitation.

When the precipitation has been effected in water, it is advantageous to keep the medium alkaline during the course of the operation, by introducing the metallates, and then the salts, into the solution of the first constituent.

As is known, the zeolites are destroyed by a medium which is acid to litmus. It has been found that their catalytic properties are largely dependent on the final P_H value of the precipitation. For example, zeolites with a lithium base are entirely inactive if the precipitation ends with a $P_H=10$, and display maximum activity at $P_H=7$.

The cohesion and hardness increase pari passu with the activity.

The artificial zeolites are prepared in a medium with a P_H value between 8 and 6.8, and in general, it is highly advantageous to terminate the precipitations very close to or precisely at a $P_H=7$, at 20° C., or at a corresponding P_H if the temperature is different since, as is known, the P_H value of water varies with the temperature.

After filtration and washing, the zeolites should be dried progressively, for example at 100° C, and then gradually heated to the temperature of reduction, treatment or catalysis. These operations should be performed with special precaution, in view of the high activity of these catalysts. For example, when the zeolite contains reducible metallates, direct reduction under pressure will destroy the activity almost completely.

The reduction is advantageously commenced at a low temperature (e.g. 200° C. for copper or manganese zeolites) and ordinary pressure, with a gas containing 5—10% of carbon monoxide diluted in an inert gas. It may then be continued, without inconvenience, under pressure (600—800 atmospheres) and at a higher temperature (300—500° C.).

EXAMPLE 1.

10 kg. of potassium permanganate are dissolved in 1200 litres of water, 8 kg. of caustic soda being added, and reduction effected with 7 litres of alcohol in the cold. The resulting manganate is treated with an addition of a solution of 4 kg. of borax, followed by an acetic acid solution i.e. sufficient acetic acid to dissolve the carbonates of:

5.500 kg. of commercial cerium carbonate

8 litres of 8° Bé aluminium acetate, and

1 kg. of malachite, with energetic stirring.

The whole is then adjusted to $P_H=7$, by means of a little (3—4 litres) acetic or formic acid. After centrifuging and washing the mass is dried at 100° C.

The crushed grains are reduced with 10% CO at 200° C., and then with 80% CO at 500 atmospheres, the temperature being raised to about 300—350° C.

A mixture of 3CO and $2H_2O$ is then passed at a space velocity of 5000—10000 (hourly flow of gas = 5000—10000 times the volume of the catalyst) over the catalyst at the same temperature and pressure as is used for the reduction, and a solution of aliphatic ethers and alcohols is collected in an amount corresponding to a degree of conversion of 40—50%.

EXAMPLE 2.

1.200 kg. of borax and 9 kg. of sodium aluminate are dissolved in 800 litres of water, and cooled with ice to 0° C. The following formic acid solution (sufficient formic acid being added to dissolve the carbonates), cooled to the same temperature, is added:

Precipitated lithium carbonate, 0.555 kg;

Dry potassium carbonate, 0.210 kg.;

Crystallised thorium formate, 2.350 kg.; and

8° Bé aluminium acetate, 2 litres.

The whole is adjusted to $P_H=7.5$ with a little formic acid, and the mass is then centrifuged, washed and dried at 100° C., no previous reduction being needed. The crushed catalyst is heated to 270—280° C., under a pressure of 900 atmospheres in a current of CO saturated with steam and with a space velocity of 2000—5000 (hourly flow of gas = 2000—5000 times the volume of the catalyst). A 20% solution of acetic acid and homologues is obtained, in an amount corresponding to a degree of conversion of 10%.

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 aliphatic organic compounds containing oxygen by the action of carbon monoxide on water in the state of liquid or vapour in which artificial zeolites resulting from the union of salts of a strongly alkaline character with metallates or salts of amphoteric metals, with or without addition of neutral, or appreciably neutral salts are employed as catalysts.

2). Method of carrying out the process set forth in claim 1, in which artificial zeolites prepared in a medium with a P_H value between 8 and 6.8, preferably very close to 7, at the close of the operation at 20° C., or with a corresponding P_H value if the temperature is different, are employed as catalysts.

3). Method of carrying out the process set forth in claim 1, in which the substances resulting from the reduction, in two phases, of artificial zeolites containing reducible compounds, the first phase of the reduction taking place at a slightly elevated temperature, near 200° C., under atmospheric pressure and with dilute reducing gas, and the second phase taking place at a higher temperature, between 300 and 500° C., under pressure and with concentrated reducing gas, are employed as catalysts.

4). The process of producing aliphatic organic compounds containing oxygen, substantially as described.

Dated this 10th day of April, 1930.

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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. 279,466 and 286,212.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 123A.—50/8/1931.]