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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to the Synthesis of Alcohols.

I, GIULIO NATTA, of 19, Via Rugabella, Milan, Italy, an Italian Subject, 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 is for improvements in and relating to the synthesis of alcohols.

The Application for British Letters Patent No. 7966 of 1929 (Specification No. 330,919) relates to the use of smithsonite as a catalyst for the synthesis of methanol.

A method has now been discovered whereby the smithsonite and other catalyst used for the synthesis of methanol can be rendered much more active and thus applicable industrially to the synthesis of higher alcohols.

This invention consists of a process for the synthesis under pressure of alcohols higher than methanol from mixtures of carbonic oxide and hydrogen, characterised by the use, as catalysts, of alkali salts of fatty acids mixed with porous supports.

In the literature regarding the synthesis, from mixtures of carbonic oxide and hydrogen, of mixtures of numerous organic products, there have been proposed as catalysts certain metals and metallic oxides mixed with alkaline hydrates, which, particularly in the case of alkalinised iron, lead to the formation of numerous products other than alcohols, such as hydrocarbons, acids, ethers, etc. and to a noteworthy loss of carbonic oxide and of hydrogen through the formation of inert gases or liquids such as methane and water.

The complex nature of these mixtures of liquids which for the greater part separate out as soon as collected in two strata detracts from the industrial value of the products. That value is consequently limited.

Moreover the greater part of the catalysts proposed present a small active surface, their porosity is limited, whilst strong concentration in alkalis can only be obtained with difficulty. For these reasons, the catalysts proposed for these syntheses are for the greater part but little active and require low velocity of the gases and, therefore, in order to obtain yields which can be compared with those obtained in the synthesis of methanol, they require large volumes of the catalysts. Moreover such catalysts often lose their activity or such activity decreases rapidly.

For these reasons the synthesis of higher alcohols from the constituents of water gas has not been applied on a large scale industrially, in contrast with the wide application of the synthesis of methanol in industry.

In the said Application for British Letters Patent No. 7966 of 1929 (Specification No. 330,919) the advantages which smithsonite offers over other catalysts in general for the synthesis of methanol, and over zinc oxide in particular, have been shown, and it was demonstrated that from the point of view of catalysis, calcined smithsonite cannot in any way be compared with artificial zinc oxide.

Summarising: the advantages of smithsonite are due to the activation by the action of the impurities present in the form of solid solutions which cannot be reproduced artificially, to the uniformly distributed porosity, to the high mechanical resistance and thermic conductivity, to the resistance to deterioration and to decrease in activity due to prolonged and continuous operation, as well as to the resistance to over heating; all of which properties are manifested in a high and lasting catalytic effect.

In the course of experiments carried out during the research for a process of synthesis of higher alcohols only, the object of the present invention, it was shown that smithsonite, previously heated to 400—500° C. (or better still at lower temperatures and under reduced pressure), is capable of absorbing, by for example, immersion in or spraying with extremely concentrated solutions of alkaline salts, notable quantities of the latter which substantially modify its valuable catalytic properties.

For example, smithsonite to which 20% by weight of potassium hydrate has been added forms a good catalyst for the synthesis of higher alcohols.

If, for example, a mixture of one volume of carbonic oxide to two or two and a half volumes of hydrogen be passed over such catalyst at a pressure of 250—300 atmospheres and a temperature of about 400° C. and with a velocity of gas corresponding to 10 cubic metres per hour (measured at ordinary pressure) per litre of gross catalytic space, a yield of about 30—35 ccs. of alcohols calculated as anhydrous for each cubic metre of gas for each passage is obtained. Under the same conditions and using catalysts formed by the reduction of a mixture of potassium chromate and basic chromate of zinc, only about 25 ccs. of anhydrous alcohols were obtained.

Of the alcohols obtained with smithsonite alkalinised as described with 20% of potassium hydrate and under the above indicated conditions, half is composed of ethyl alcohol and propyl alcohols, the latter preponderating to no small degree, and not more than 20—25% of methanol. Moreover butyl alcohols and small percentages of amyl alcohols besides alcohols higher than the amyl alcohols are present. Their relative percentages may vary according to the duration of the contact of the gas with the catalyst, and also according to the age of the catalyst. It should, however, be noted that sensible quantities of organic products other than alcohols were not obtained, and that there is no formation of hydrocarbons, liquid or gaseous, not even of methane. It is only when the starting gas contains small quantities of methane that the methane is found concentrated in the residual gas, after the almost complete combination of the carbonic oxide with the hydrogen.

Important modifications in this process for the synthesis of higher alcohols from the constituents of water gas and which also form part of the present invention, have been arrived at by the interpretation of the formation of alcohols according to the following reactions :—

1. $CO+2H_2=CH_3OH$
2. $CH_3OH+KOH=CH_3OK+H_2O$
3. $CH_3OK+CO=CH_3COOK$
4. $CH_3COOK+2H_2=CH_3CH_2OH+KOH$

which justify the relation that has been found to subsist between the catalytic activity of the alkali and its basicity, and explain the harmful action exercised by carbon dioxide only in the synthesis of the higher alcohols and not in the synthesis of methanol. The reactions (2), (3) and (4) may be repeated for those alcohols, higher than methanol, which form in stages.

The harmful action of carbon dioxide is explained by the equation :—

$$CO_2+H_2=CO+H_2O \quad . \ . \ . \ (5)$$

which contrary to that which takes place at ordinary pressure, I have found to be strongly displaced towards the right at 400—450° C. and at high pressure with the formation of water which causes the retrocession of the reaction (2) and corresponding non-formation of the higher alcohols.

The formation of alkali salts of fatty acids has been experimentally observed in catalysts alkalinised with caustic alkalis after a certain period of time during which they were in contact with hydrogen and carbonic oxide under the conditions for the synthesis of the higher alcohols. A solution of potassium acetate, and formate, mixed with salts of higher acids such as butyric acid, etc. is obtained by washing the catalyst with water.

An excellent process for the synthesis of higher alcohols results from the employment of catalysts composed chiefly of or activated by salts of fatty acids, such as the formates, acetates, propionates, etc. of alkali metals, particularly potassium, rubidium and caesium. However, such salts cannot, in the pure state, be alone practically applied as catalysts in this synthesis because they melt at the temperature of reaction.

An excellent catalyst may be obtained by soaking porous substances such as zinc oxide, pumice stone, magnesite, silica, and above all smithsonite, heated at low temperatures or in a vacuum, in saturated solutions in the hot, of such salts.

The results obtained, for example, with smithsonite activated with potassium acetate, are much better than those obtained with smithsonite activated with an equivalent quantity of potassium hydrate. With a catalyst containing 18% by weight of potassium acetate and at a temperature of 400—420° C. and pressures of 250—300 atmospheres under conditions analogous to those previously indicated, and with an hourly velocity of gas of 10 cubic metres measured at ordinary pressure for each litre of catalytic space, about 45 ccs. of anhydrous alcohols for each cubic metre of gas were obtained for each passage. The yield was almost 50% more than that obtained with the same smithsonite alkalinised with 20% of potassium hydrate and therefore containing about double the number of atoms of potassium.

A greater quantity of still higher alcohols was also obtained. Of these more than 6—7% boiled at temperatures of over 150° C. and a notable fraction boiled at about 210° C.

After several days of operation the catalyst still possesses a high catalytic activity, and it is observed that the greater part of the potassium acetate is unaltered; only part is changed into salts of higher fatty acids. In order to avoid the decomposition of these fatty acid salts, which would take place spontaneously at the temperature of reaction if the catalyst were heated to that temperature at ordinary pressure it is necessary for the starting of the reaction first to increase the pressure and then the temperature.

Under these conditions there is only an insignificant decomposition of the catalyst, as is shown by causing pure hydrogen to circulate at high pressure and temperature. It is only by causing large quantities of hydrogen to circulate over long periods of time that one can succeed in forming small quantities of alcohols and of water. This is probably due to partial decomposition of the organic salt which cannot regenerate owing to the lack of carbonic oxide in the gas.

Having observed that the formation of higher alcohols occurs with methanol as an intermediate compound, and having noted that the catalysts suitable for the synthesis of higher alcohols are not very active in the synthesis of methanol, it has been found that greater transformations of gas into alcohols can be obtained by passing the gas alternately over catalysts for methanol, smithsonite for example, and over catalysts for higher alcohols, for example, smithsonite alkalinised with alkali salts of fatty acids. This procedure may be realised experimentally either by filling the same reaction chamber with two or more alternating layers of the two catalysts, or by using granulated catalysts and mixing together the two types of catalysts which each exercise their functions in the synthesis, increasing the total yield.

The selective action of the catalyst as regards the alcohols produced also varies according to the fatty acid used, it being possible to obtain a greater percentage of higher alcohols with very active catalysts. The velocity and, above all, the composition of the gas also influence the operation.

With gases that are very rich in hydrogen, the reactions which lead to the formation of alcohols only and water preponderate:—

$$nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O \quad \ldots\ldots (6)$$

There is a notable and contemporaneous formation of CO_2, with gases that are rich in carbonic oxide. However, I do not believe, as some have supposed, that the following reaction occurs:—

$$(2n-1)CO + (n+1)H_2 = C_nH_{2n+1}OH + (n-1)CO_2$$

but rather that the CO_2 forms successively through the action of the steam generated in the reaction (2) or in reaction (6) thus causing the reaction:—

$$CO + H_2O = CO_2 + H_2$$

to be displaced towards the right.

It has been found that the presence of an excess of carbon dioxide, although it does not harm the synthesis of methanol beyond leading to a higher consumption of hydrogen and to the production of crude methanol which is richer in water, is on the contrary most harmful in the synthesis of the higher alcohols. By using a gas containing 15—20% of CO_2, methanol and water are formed almost exclusively with only traces of higher alcohols, even though the same catalysts be used which in the absence of, or in the presence of small percentages of CO_2 produce high percentages of such higher alcohols.

By eliminating, during the high pressure cycle, the carbon dioxide which forms during the synthesis of the higher alcohols, it is possible to obtain a greater yield of the latter whilst the hydrogen is utilised to a better purpose as it is not consumed uselessly to form water.

Whilst by using a gas containing about 10% of carbon dioxide the whole of the water formed during the synthesis reaction (2) and (6) of the higher alcohols is found again mixed with the latter during condensation, by operating in the absence of CO_2 that water reacts with the carbonic oxide and regenerates hydrogen and forms carbon dioxide.

By continuously eliminating this water, it is possible to realise a process which allows of quantitatively obtaining higher alcohols from a mixture of carbonic oxide and of hydrogen, containing less hydrogen than would be calculated from the reactions (1) and (4) and therefore more similar in composition to normal water gas. The excess of carbonic oxide is eliminated during the synthesis itself by transforming it into carbon dioxide.

Washing with water alone, in order to eliminate completely the carbon dioxide during the high pressure cycle, is not sufficient unless large quantities of water are used which also take up sensible quantities of the other gases. It has been found that it may be convenient to effect the washing with the same synthetic methanol in which, as is well known, carbon dioxide is much more soluble than in water. The evolution of the dissolved carbon dioxide when the pressure is released may supply a notable source of refrigerating action that can be utilised to cool the gas under pressure and to favour the absorption itself of the carbon dioxide by the methanol used in washing. Washing the gases with methanol also offers the advantage of eliminating certain harmful impurities from the gas such as $Fe(CO)_5$, which, in the synthesis of methanol may in time deteriorate the catalyst, and of dehydrating the gas. In this way purer products and higher yields are obtainable.

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. A process for the synthesis under pressure of alcohols higher than methanol from mixtures of carbonic oxide and hydrogen, characterised by the use, as catalysts, of alkali salts of fatty acids mixed with porous supports.

2. A process as in Claim 1, characterised by the fact that salts of fatty acids of the metals of the potassium group (potassium, rubidium, caesium) or mixtures of the same are used as catalysts.

3. A process as in Claim 2, characterised by the use of potassium formate as catalyst.

4. A process as in Claim 2, characterised by the fact that potassium acetate is used alone or mixed with potassium formate, as catalyst.

5. A process as in any of the Claims 1 to 4, characterised by the fact that a catalyst suitable for the synthesis of methanol is used as a support.

6. A process as in any of the Claims 1 to 4, characterised by the fact that any of the above mentioned alkali salts of fatty acids is employed as catalyst in the presence of another catalyst which is suitable for the synthesis of methanol alone, for example, smithsonite, impregnated with the said salt.

7. A process as in any of the Claims 1 to 6, characterised by the fact that a mixture of carbonic oxide and hydrogen in admixture with synthetic methanol is used.

8. A process as in any of the Claims 1 to 7, characterised by the fact that the operation is commenced with mixtures containing more than two volumes of hydrogen for every volume of carbonic oxide.

9. A process as in any of the Claims 1 to 8, characterised by the fact that a washing or absorption apparatus, for the elimination of the carbon dioxide produced by the reaction, is introduced into the cycle of circulation of the gases under pressure.

10. A process as in Claim 9, characterised by the fact that the gases undergo a process of washing with alcohols or mixtures of alcohols under pressure.

11. A process as in Claim 10, characterised by the fact that the washing is effected with synthetic methanol.

12. A process as in Claims 9, 10 and 11, characterised by the fact that the process may be rendered continuous, by the circulation, and return in cycle, under pressure, of the gases remaining after catalysis, even though the initial mixture of gas contains less than two volumes of hydrogen for every volume of carbonic oxide.

13. The improved process for the synthesis of alcohols, substantially as described.

14. Alcohols and other products whenever manufactured by a process as hereinbefore described and claimed.

Dated this 16th day of October, 1929.

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