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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in the Hydrogenation of Carbon Monoxide to produce Hydrocarbons having more than one Carbon Atom in the Molecule

I, Harold Edwin Potts, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention, which has been communicated to me by N.V. Internationale Koolwaterstoffen Synthese Maatschappij (International Hydrocarbon Synthesis Company), a Dutch Company, of 20, Wassenaarscheweg, The Hague, Holland, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

For the production of carriers for catalysts for the hydrogenation of carbon monoxide for the synthesis of hydrocarbons having more than one carbon atom in the molecule mainly diatomaceous earth is used.

In view of its content of organic and inorganic impurities it cannot be used as quarried but must be refined. In order to free it from organic substances it was hitherto considered to be indispensable to subject it first to a calcination, for which temperatures of at least 600° Centigrade were used. In this operation a considerable sintering of the large surface of the diatomaceous earth is liable to take place. Simultaneously a part of the inorganic impurities is usually rendered insoluble. This preliminary calcination of the diatomaceous earth was hitherto also carried out in those cases, where for the removal of the inorganic substances, in particular of iron and aluminium compounds, a treatment with acid was carried out. The part of the inorganic impurities which in the calcination had been rendered insoluble could, however, not be removed. Another method by which attempts have been made to avoid difficulties due to the presence of inorganic impurities arising in the employment of diatomaceous earths in the synthesis consists in the application of very high temperatures in the calcination, for example, of 900 to 1000° Centigrade, whereby all the inorganic impurities are converted into a practically insoluble form, and consequently are fixed in the diatomaceous earth. All diatomaceous earths which have been thus treated, however, still have drawbacks when employed as carriers for catalysts in the hydrogenation of carbon monoxide. One drawback is that the products, which have undergone a calcination at temperatures above 600° Centigrade, in consequence of their being sintered give catalysts of insufficient activity. A drawback of the products calcined at very high temperatures is that the fixed inorganic constituents contained therein have an injurious effect on the catalyst in the hydrogenation of carbon monoxide.

It has now been found that improved results in the production of hydrocarbons having more than one carbon atom in the molecule by hydrogenating carbon monoxide in the presence of catalysts comprising a diatomaceous earth carrier are obtained if the catalyst is prepared by first leaching crude diatomaceous earth with acids which boil at about 120° C. or therebelow, washing and drying and freeing said diatomaceous earth from organic substances by calcination at temperatures, at which a sintering of the diatomaceous earth does not yet take place. Suitable temperatures for the said calcination are those between 500° and 550° Centigrade. The use of acids of the nature specified has the advantage that in the subsequent heating all of the acids which still remain in the substance after washing are completely vaporised. Nitric acid or hydrochloric acid may, for example, be used, but also gaseous acids such as carbonic acid. The improvement obtained is not only due to the fact that in the removal of the organic substances by calcination too high temperatures are avoided, but that prior to the calcination the inorganic substances are removed so that they cannot become insoluble and fixed in the diatomaceous earth.

The advantages obtained in the hydrogenation of carbon monoxide in accordance with the invention are the following:

In consequence of the avoidance of too high temperatures during the calcination, the original surface and shape of the

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crude diatomaceous earth are maintained. Moreover the strength of the catalysts produced with the diatomaceous earth treated in accordance with the invention is so great that in the usual test they only give half of the abrasion of that of catalysts which are obtained with a diatomaceous earth refined by the known methods. Due to the increased strength the formation of dust from the catalysts which may occur when transferring the catalysts from one vessel to another is substantially lowered, whereby a remarkable improvement in the conduct of the catalytic operation is obtained, since a uniform passage of the synthesis gas and a contacting of all parts of the catalyst mass with uniform amounts of gas is secured. Further, by the use of the diatomaceous earth treated in accordance with the present invention an increase in the lifetime of the catalyst is obtained. This is shown by the fact that under similar reaction conditions (about 186° Centigrade and 1 atmosphere) with a proportion of $CO : H_2$ of 1 : 2 after about 1000 hours of operation with the hitherto usual catalysts a yield of only 105 grams or less per cubic metre is obtained whereas with the new catalysts after the same period of time the yield still amounts to 122 grams per cubic metre. The catalysts produced with the purified diatomaceous earth also have advantages due to the fact that in the regeneration of the catalyst no extraneous metals dissolve from the carrier.

The following Examples will further illustrate how the invention may be carried out in practice but it should be understood that the invention is not limited to the said Examples.

EXAMPLE I.

In the hydrogenation of carbon monoxide improved results were obtained by using a catalyst comprising diatomaceous earth which had been prepared as follows:—

200 grams of a crude diatomaceous earth having a water content of about 50 per cent. were heated at a temperature of 50 to 60° Centigrade under continuous stirring in 2 litres of nitric acid of 5 per cent. during two hours. Hereupon the earth was filtered, washed with hot water and after drying calcined for one hour at 600° Centigrade.

EXAMPLE II.

A further method of preparing the diatomaceous earth was as follows:—

100 grams of crude diatomaceous earth containing about 50 per cent. of water were made into a suspension with 2 litres of water. Into this suspension a strong stream of carbonic acid was led while cooling. After two hours, it was separated by filtration from the formed bicarbonates of iron and calcium which were in solution, washed for a short time with cold water and dried. After the drying the diatomaceous earth was heated for one hour at 550° Centigrade for the removal of organic substances.

EXAMPLE III.

Two catalysts composed of 100 parts of cobalt, 15 parts of thorium dioxide and 200 parts of diatomaceous earth were produced. As diatomaceous earth in one case the normal commercial diatomaceous earth having an apparent specific gravity of 0.12 was used, in the other case a crude diatomaceous earth which had been pretreated by treatment with nitric acid and calcination in accordance with the present invention. Both catalysts were reduced in the same manner at 350° Centigrade and synthesis gas passed thereover at 185° Centigrade. During the first 700 hours of operation the yield with the two catalysts remained the same. During the following period of operation, namely the 700th to 1200th hour, the yield with the catalyst prepared with diatomaceous earth refined in accordance with the present invention was 10 per cent. higher. During the third period of operation, namely the 1200th to 1600th hour, the yield of the catalyst prepared with diatomaceous earth in accordance with the present invention was more than 15 per cent. higher than that with the other catalyst.

	Yield in grams per m³ ideal gas ($2H_2 : 1\ CO$) after 1600 hours of operation.		
	Oil	Benzine	Total liquid products
Catalyst with commercial diatomaceous earth (sp.gr.0.12)	73	38	111
Catalyst with purified diatomaceous earth	77	51	128

EXAMPLE IV.

Two catalysts with the following composition were produced: 100 parts of cobalt, 15 parts of thorium dioxide, 100 parts of diatomaceous earth. As diatomaceous earth in one case again the normal commercial diatomaceous earth (sp.gr.0.12) was used and in the other case a diatomaceous earth purified in accordance with the present invention. The superiority of the latter became quickly apparent during employment in a synthesis carried out at 185° to 187° Centigrade by the yields obtained:

Duration of treatment	Average yield of liquid products in grams per cubic metre of ideal gas ($2\ H_2:1\ CO$,		
	–700 hours of operation	700—1200 hours of operation	1200—1600 hours of operation
Catalyst with commercial diatomaceous earth (sp.gr.0.12) - - - - - - - -	117 -	93 -	93
Catalyst with diatomaceous earth refined in accordance with the present invention	121 -	113 -	115

In British specification 484,828 improvements are described in the manufacture of ebonite and the like, especially suitable for electrical purposes, which improvements comprise applying silica known as kieselguhr, infusorial earth and diatomaceous earth, which have been wholly or substantially freed from electrically detrimental impurities, for example, by washing with acid and/or calcining. Preferably, according to this specification the kieselguhr is subjected to both the acid washing and calcination treatments, and the preferred temperature is about 550—600° C.

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. Improvements in the production of hydrocarbons having more than one carbon atom in the molecule by hydrogenation of carbon monoxide in presence of catalysts comprising diatomaceous earth as a carrier characterised in that the carrier is obtained by leaching crude diatomaceous earth with acids which boil at about 120° Centigrade or therebelow, washing, drying and freeing said diatomaceous earth from organic substances by calcination at temperatures, at which a sintering of the diatomaceous earth does not yet take place.

2. In the process as claimed in claim 1, leaching the diatomaceous earth with nitric acid.

3. In the process as claimed in claim 1, leaching the diatomaceous earth with hydrochloric acid.

4. In the process as claimed in any of claims 1 to 3, carrying out the calcination at a temperature between 500 and 550° Centigrade.

5. Improvements in the production of hydrocarbons substantially as described in Examples 3 and 4.

6. Hydrocarbons when obtained in accordance with any of the preceding claiming clauses.

Dated this 21st day of November, 1939.

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