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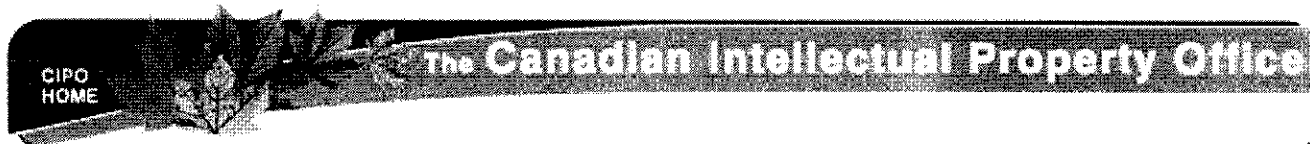
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(12) Patent:

(54) PROCESS FOR THE PRE-TREATMENT OF IRON-CONTAINING CATALYSTS FOR THE HYDROGENATION OF CARBON MONOXIDE

(54) PROCÉDE POUR LE TRAITEMENT PREALABLE DE CATALYSEURS CONTENANT DU FER POUR L'HYDROGENATION D'OXYDE DE CARBONE

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ABSTRACT:

CLAIMS:

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Iron catalysts, such as are used, for example, for the hydrogenation of carbon monoxide at medium or high gas pressures, are pre-treated with reducing gases before being used. In this manner, a more or less extensive  
5 reduction, and/or a forming of the catalysts is attained according to the kind of gas used, which considerably affects its activity. Gases suitable for the reduction process proper are those consisting mainly of hydrogen. In contrast to this, for catalyst forming, carbon mono-  
10 xide-containing gases are required, and, in a required case, even the use of pure carbon monoxide is desirable. Up to the present, in the reducing pre-treatment of iron catalysts low gas velocities were used, which at atmospheric pressure amounted to approximately 2-40 cm. per second.  
15 Furthermore, treatment of catalysts had hitherto to be effected with catalyst-layers of relatively little thickness in order to obtain uniform catalyst characteristics.

It has been found that the pre-treatment of iron catalysts can be effected considerably more economically,  
20 and considerably improved catalyst characteristics can be obtained, if high gas velocities of 50-500 cm. per second, preferably gas velocities of 100-200 cm. per second are used. In such conditions, the layer thickness of the catalyst can be increased several times in the usual  
25 reduction apparatus. At low gas velocities considerable differences develop in the reduction value of the catalyst in the upper and lower layers of the catalyst filler with layer thicknesses of about 100 cm. These differences do not disappear even if the reduction period is considerably  
30 extended. This fact adversely affects the synthesis behaviour of iron catalysts.

If the increased gas velocities according to the invention are used, practically the same reduction value is obtained within a short time, for example, after only 30 minutes, both in the upper and in the lower parts of a catalyst layer of 100 cms. thickness. The layer thickness of the catalyst can be still further increased, if required, so that this kind of reducing pre-treatment of catalysts is economically of great advantage.

A further disadvantage in the low velocity of the reduction gases used hitherto consists in the fact that the lower catalyst layers, due to the high partial pressure of the water vapour prevailing in the reduction gases led in from above, have their catalytic activity and duration of life to some extent adversely affected; this does not occur when high gas velocities are used.

Iron catalysts pre-treated according to the process of the invention have the advantage that in the carbon monoxide hydrogenation the synthesis temperature can be considerably lowered without reducing the extent of conversion. In the carbon monoxide hydrogenation, iron catalysts require, as their period of use increases, a gradual increase in the reaction temperature. The lower starting temperature of catalysts pre-treated according to the invention provides an increased useful temperature difference in connection with the gradual temperature increase referred to above, which is of great importance for the increased length of catalyst life.

Furthermore, by means of the iron catalysts pre-treated according to the invention, the formation of high molecular hydrocarbons, particularly the production

of synthetic products boiling above  $320^{\circ}\text{C}.$ , can be considerably increased. At the same time, a considerable reduction in the formation of methane takes place, which in some cases decreases to less than half the usual quantities formed in known processes. There is also an improvement in the  $\text{CO}/\text{H}_2$  consumption ratio of the synthesis gases passed through.

If water gas is used, and only passed once over the catalyst, i.e. used without re-cycling, frequently no useful gas-consumption is obtained with iron catalysts, which were reduced in the manner hitherto usual. In the majority of such cases considerably less hydrogen is used up than is present in the gas mixture. Iron catalysts pre-treated according to the invention do not have this disadvantage, but show a considerably increased hydrogen consumption so that, in the process of the invention, even water gas can be usefully consumed in a single passage over the catalyst.

The fact that a lowering of the synthesis temperature can be attained is of particular advantage with catalysts which chiefly produce oxygen-containing products, that is to say, which have a comparatively high alkali content of 1% - 10%, preferably from 4% - 8% (calculated as  $\text{K}_2\text{O}$ ). The formation of oxygen-containing carbon compounds is improved by low synthesis temperatures, so that iron catalysts, pretreated according to the invention, effect an increased yield in oxygen-containing products.

With iron catalysts pretreated according to the invention, the catalyst load also can be increased far above the normal load of 100 litres of synthesis gas per litre of catalyst volume which is the normal load used up to the present. In order to obtain the same conversion

As, it is necessary to increase the synthesis temperature accordingly. In the pre-treatment of iron catalysts hitherto usual, such an increase in the synthesis temperature nearly always resulted in a high increase in methane formation which, in some circumstances, increase so much that the synthesis became uneconomical. In contrast to this, the new catalysts treated according to the process of the invention, at increased loads, keep the methane content down to economically reasonable limits.

In order to obtain particularly good catalyst characteristics, care has to be taken that the gases used in the reducing pre-treatment contain neither carbon dioxide nor water vapour.

EXAMPLE 1.

A catalyst containing 5 parts copper per 100 parts iron was precipitated with soda solution from a solution which contained corresponding quantities of iron nitrate and copper. After careful washing, the precipitated mass was impregnated with potassium silicate and then dried. The impregnated mass preferably contains  $3K_2O: 7.5 SiO_2$  for 100 Fe. The catalyst was then reduced with a gas mixture which consisted of three parts by volume of hydrogen and one part by volume of nitrogen. The gas velocity was 140 cm. per second, calculated under normal conditions, and the temperature was  $300^{\circ}C$ . After a reduction period of 90 minutes the catalyst had a reduction value which corresponded to approximately 40% free iron.

If a catalyst, pretreated in this manner, is used for the synthesis with water gas at a load of 100 litres of gas per litre of catalyst per hour and  $10 \text{ kg/cm}^2$  pressure, a conversion of 65% ( $CO + H_2$ ) is obtained at  $209^{\circ}C$ . The methane formation amounts to approximately 6%. The liquid products contain approximately 65% hydrocarbons boiling above  $320^{\circ}C$ .

If an iron catalyst of the same composition is reduced, in the manner hitherto usual, with a gas velocity of only 45 cm. per second, then considerably more time is needed to obtain an equally high reduction value. These catalysts yield only a conversion of 60% in the subsequent synthesis with water gas at the normal load of 100 litres of gas per litre of catalyst per hour, in spite of the synthesis temperature being increased to 215°C. The methane formation then amounts to 7% - 8%. Only 59% of hydrocarbons boiling above 320°C. are contained in the liquid synthetic products.

EXAMPLE 2

An iron catalyst produced and pretreated according to Example 1, which had received a somewhat higher impregnation with alkaline silicate (4.5 K<sub>2</sub>O: 10.5 SiO<sub>2</sub> for 100 Fe), was loaded in the synthesis operation with 300 litres water gas per litre of catalyst per hour. This load was approximately three times as high as the usual normal load.

At a synthesis temperature of 226°C. and a synthesis pressure of 10 kg/cm<sup>2</sup> the (CO + H<sub>2</sub>) conversion amounted to 65%. 60% of the synthetic products boiled above 320°C. (paraffin yield). The methane formation was approximately 7%.

If an iron catalyst of the same composition is reduced under the present usual conditions, that is to say, with a gas velocity of approximately 30-40 cm. per second (measured linearly), the reaction temperature has to be increased to 238°C. in order to obtain the same conversion. Under such conditions the methane formation amounts to 10% - 11%. The yield in high molecular hydrocarbons was reduced to approximately 55% of the liquid synthetic products.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the pre-treatment of iron-containing catalysts with gases containing at least one of hydrogen and carbon monoxide, said catalyst pre-treatment being carried out with catalyst layers  
5 of a thickness of at least approximately 100 centimeters and at high gas velocities of approximately 50 to 500 centimeters per second.
2. A process as defined in claim 1, wherein  
10 the thickness of the catalyst layers lies in the range of 80 to 400 centimeters and the gas velocities are in the range 100 to 200 centimeters per second.
3. A process as defined in claim 1, wherein  
the iron catalysts contain 1 to 10% alkali calculated  
as  $K_2O$ .
- 15 4. A process as defined in claim 3, wherein the iron catalysts contain 4 to 8% alkali calculated as  $K_2O$ .
5. A process as defined in claims 1, 2 or 3,  
wherein the said gases used in the pre-treatment are  
freed as far as possible from their water content.
- 20 6. A process as defined in claim 1, wherein the said gases used in the pre-treatment are freed as far as possible from their water content.
7. A process as defined in claim 3, wherein the  
said gases used in the pre-treatment are freed as far  
25 as possible from their water content.
8. A process as defined in claims 1, 6 or 7,  
wherein the said gases used in the pre-treatment are  
previously freed as far as possible from their carbon  
dioxide content.