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(54) PROCESS FOR CARBON MONOXIDE HYDROGENATION

(54) PROCEDE POUR L'HYDROGENATION D'OXYDE DE CARBONE

(72) Inventor (Country):	WALTER ROTTIG (Not Available)
(73) Applicant (Country):	RUHRCHEMIE AKTIENGESELLSCHAFT
(71) Applicant (Country):	
(74) Agent:	
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In carbon monoxide hydrogenation carried out at atmospheric pressure (synthesis at normal pressure), the use of iron contacts is known. These contacts nearly always contain, in addition to iron, small amounts of copper, and frequently also appropriate activators, for example calcium or zinc. Contacts of this type always show a more or less high alkali content, for example in the form of soda, sodium hydroxide, potassium hydroxide or potassium carbonate.

The quantity of alkali present, usually calculated as K_2O , is of fundamental importance. If small quantities of alkali are used, for example 0.5%-1%, calculated on the total iron content (Fe), the proportion of high molecule hydrocarbons in the products is relatively small. On the other hand, the methane formation is fairly high. If the quantity of alkali is raised to 5% - 10% K_2O , then there results an appreciably higher yield of high molecule hydrocarbons, whilst the methane formation decreases. These contacts quickly become coated with paraffin during the reaction, and this results in a speedy reduction of their activity, and often necessitates the extraction of the contacts at short intervals.

In catalytic carbon monoxide hydrogenation, particular importance is attached to a low content of high molecule hydrocarbons. It was found that this object can be achieved at normal pressure, or at a pressure only a few atmospheres higher, when iron contacts are used, if catalysers are employed which are impregnated with alkali salts, in particular potassium salts of pronounced acid characteristics, instead of with alkali hydroxide or alkali carbonate. Particularly good contact properties

result when the impregnation of the contacts is carried out by means of alkali silicate, primary alkali phosphate and/or primary alkali borate. By contrast, secondary phosphates are not suitable, since their acid component is not sufficiently pronounced, and therefore, if they are used for the impregnation of the contacts, they cause a considerably higher formation of high molecule hydrocarbons.

If the impregnation of the contacts is carried out by means of alkali silicate a K_2O/SiO_2 ratio in the region of approximately 1:3 to 1:6 is particularly advantageous. With an increase in the silicate components beyond this, the contact shows a marked decrease in activity. The increase of the alkali components in such a manner that for 1 part K_2O there are precipitated less than 3 parts SiO_2 , causes an appreciably stronger paraffin formation.

The iron contacts according to the invention, under severe synthesis conditions, for example when working at the highest possible conversion by the use of appropriate reaction temperatures, show only a small paraffin formation; nevertheless, surprisingly enough, the methane formation also remains relatively low. Also, under less severe working conditions, no particularly large quantities of paraffin result. In these cases the methane formation decreases still further.

To obtain the highest possible yield of hydrocarbons of low boiling point, whose molecule size lies, for example, between C_5 and C_{12} , the iron contacts to be used according to the invention are, with advantage, reduced at relatively low temperatures, by means of hydrogen, and by the use of high gas velocities. The reduction

temperatures are preferably chosen between 220°C. and 250°C. The gas velocities are from 1 to 1.5 metres per sec. An alteration of these reduction conditions produces iron contacts which either have a lower activity, or cause an increased methane formation. If the reduction is effected by water gas instead of hydrogen, then, in that case the objectionable formation of high molecule hydrocarbons again increases.

The iron contacts according to the invention are best prepared completely without, or with only a small content of the usual carrier substances (for example, Kieselguhr).

Example

A contact consisting of 100 parts iron and 5 parts copper was precipitated hot, in known manner, from the appropriate nitrate solutions by means of soda solution. Immediately after the precipitation, the mother solution was filtered off, and the alkali still present in the filter cake was washed out with condensate water until there was a residual content of approximately 0.8% K₂O. The contact cake, still damp, was then impregnated with a water-glass solution containing approximately 3 parts SiO₂ per 1 part K₂O. After this impregnation, the damp contact mass, calculated on the total iron present, contained 25% SiO₂. The superfluous alkali was washed out by neutralization with dilute nitric acid and subsequent filtration, leaving a K₂O/SiO₂ ratio of 1:5.

The contact mass was next dried for 24 hours at 110°C., and then sieved to a particle size between 1 and 3 mm. The subsequent reduction was carried out by means of hydrogen at 225°C. for a reduction period of 60 minutes, at a gas-flow velocity of 1.2 metres per sec. The contact produced in this way had a reduction value of 30% free iron.

This contact was used, in a synthesis oven, for the conversion of water gas, in such a way that each part by volume of the contact was hourly impacted with 100 parts by volume of water gas at 220°C. In this way
5 a conversion ($\text{CO}+\text{H}_2$) of 72%-74% was attained, corresponding to a 95%-98% carbon monoxide consumption. The methane formation approximated to 7%-8% of the total conversion. The consumption ratio (CO/H_2) amounted to approximately 1:0.7. The yield of Nm^3 of ideal gas
10 reached 142 g. of synthesis products without methane.

In comparison with this, an iron contact, which had received, instead of a silicate impregnation according to the invention, a corresponding impregnation with KOH, attained a yield of 138 g. per Nm^3 of ideal
15 gas. As a result of the high amount of free alkali, the conversion fell however, to 47%, whereupon an extraction was necessary to restore the full contact activity.

When the contact was impregnated according to the invention in such manner that it contained, at
20 almost the same $\text{K}_2\text{O}/\text{SiO}_2$ ratio, only 1% alkali (reckoned as K_2O), then there resulted, with approximately the same conversion, a methane formation of about 14%. The yield fell, in this instance, to 130 gms. of synthesis product per Nm^3 of ideal gas. This yield was, however,
25 maintained only at the beginning, since the methane formation, even after a relatively small running time, rose to about 15%-20%, whereupon the yield fell still more to 120 gms. per Nm^3 of ideal gas.

When the contact was impregnated in such a way
30 that there was a $\text{K}_2\text{O}/\text{SiO}_2$ ratio of 1:3, then the synthesis yielded larger quantities of high molecule hydrocarbons.

Further, in this case, after a relatively short time an extraction of the paraffin coated contact was necessary.

When the contact according to the invention was reduced with water gas instead of hydrogen then, in this case also, there was an increased paraffin yield. Furthermore, the contact had a shorter life than when the reduction was carried out with hydrogen.

When the given amount of SiO_2 was increased, contacts resulted, which under similar working conditions, showed an appreciably reduced activity, so that the conversion fell to about 60%-63%.

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

1. In a process for carbon monoxide hydrogenation, the improvement which comprises utilizing in the synthesis step an iron contact impregnated with an alkali salt of pronounced acid characteristic.
2. A process as defined in claim 1, said alkali salt being at least one of alkali silicate, primary alkali phosphate and primary alkali borate.
3. A process as defined in claim 1, said alkali salt being a potassium salt.
4. A process as defined in claim 1 or 2, wherein the contact impregnation has a K_2O/SiO_2 ratio lying in the range of approximately 1:3 to approximately 1:6.
5. A process as defined in claim 1 or 2, wherein said contact has been reduced at a linear gas velocity of 1 - 1.5 M/sec., and at a temperature in the range 220°C.- 250°C., by means of hydrogen.

Alex. E. MacRae & Co.,

P. O. Box 1077,

Ottawa, Ontario, Canada,

Patent Agents for Applicant.