

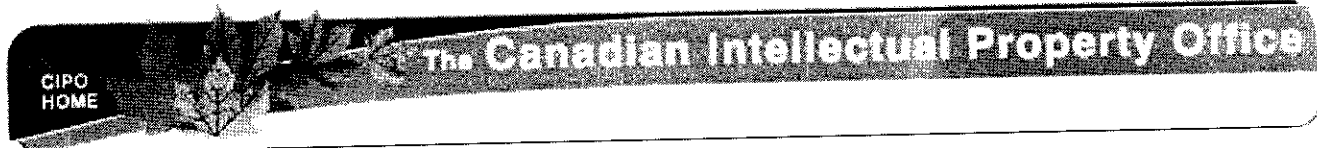


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(12) Patent:

(54) IRON CATALYST FOR THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE
 (54) CATALYSEUR FERRIQUE POUR L'HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

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This invention relates to new and useful improvements in iron catalyst for the catalytic hydrogenation of carbon monoxide.

In the catalytic hydrogenation of carbon monoxide with iron catalysts, it is desired to achieve not only a high rate of conversion but also the best possible proportionate utilization of the synthesis gases, i.e., carbon monoxide and hydrogen are to be utilized in substantially the proportion in which they are present. Furthermore, it is desired to obtain the highest possible catalyst load and the lowest possible methane formation. The iron catalyst used may be carrier containing or substantially carrier-free catalysts. Diatomaceous earth is a preferred carrier material, while in special cases, however, other materials such as activated aluminum oxide, bleaching earth, and similar materials may be used.

Carrier containing iron catalysts possess a fairly good utilization ratio at synthesis pressures in excess of about 5 - 10 kg per square centimeter which ratio may become almost proportionate when reacting, for example, water gas, and giving conversions of up to 60% (CO + H₂). The dilution of the catalyst metal caused by the carrier material requires, however, a fairly high synthesis temperature in order to attain such a high conversion rate. When using a gas load of about 100 parts per volume of gas per liter catalyst material which is conventionally considered normal, it is necessary to maintain synthesis temperatures of approximately 250°C. If the gas load is increased, however, to a multiple of the normal load, the synthesis temperature has to be increased to such a large extent that the synthesis process becomes uneconomical by reason of the increased formation of methane and deposit of carbon.

When using substantially carrier free iron catalysts, the synthesis may be carried out at temperatures which are approximately 30-40°C. lower than those required for carrier containing catalysts. With a straight passage of the synthesis gases, the load may be increased under such conditions to a value of 10 - 20 times that of the above-referred to normal load, and yet permitting the obtaining of a conversion (CO+H₂) of up to 70%. This does involve the disadvantage, however, that the substantially carrier free iron catalysts will cause to an appreciable extent a conversion of the individual gas components. Consequently, the remaining residual gas is so rich in hydrogen that it is impossible either directly or with the use of subsequently cut in synthesis stages to obtain an increase of the conversion rate up to about 90% (CO+H₂) and higher.

In the production of iron catalysts, various individual expedients are known either as such or in combination for the purpose of improving the synthesis characteristics. It has thus been proposed to obtain the precipitation of the catalyst metal from hot metal nitrate solutions with hot caustic solution while substantially maintaining predetermined hydrogen iron concentration. It has been further found that it is possible to influence the synthesis characteristics of iron catalysts to an appreciable extent by their impregnation with alkali compound, and preferably with potassium compounds. In the practice of this expedient, potassium water glass has been used for the impregnation. If an iron catalyst is, for instance, impregnated with 8 - 10 parts K₂O and 40 - 50 parts SiO₂ for each 100 parts of its iron content, it is possible to obtain at temperatures between 220 and 240°C. and substantially normal load and recycling of the gases,

conversion rates of about 60,- 70 (CO+H₂). With increased load, however, as for example a load ten times that of normal, entirely too much methane is formed, and at the same time undesired carbon deposit may occur. Iron catalysts have also
5 been impregnated in such manner that about 1 - 1.5 parts of K₂O and 3 - 5 parts of SiO₂ result for every 100 parts of iron. Though it was possible to operate such catalysts with increased gas load, an unsatisfactory proportionate utilization was obtained and a high methane formation.

10 It has been still further proposed for the purpose of improving the synthesis characteristics to apply to the reduction of the iron catalysts a variety of different methods operating with high as well as low reduction temperatures. In the practice of these expedients, partly high velocities
15 and partly low velocities of the reduction gases have been used. Still further, the composition of the reduction gases has been widely varied, using substantially pure hydrogen as well as carbon monoxide-hydrogen mixtures, and in special cases pure carbon monoxide.

20 With all these hitherto known combinations of these preparation expedients, it has been up to now impossible to obtain iron catalysts combining satisfactorily a high gas load capacity, high conversion capacity, a capacity for proportionate utilization of the synthesis gases, and a
25 low methane formation.

It has been discovered that it is possible to obtain with an entirely novel combination of as such known individual expedients, iron catalysts which will convert, for example, water gas at a gas load of 10 - 20 times that of
30 normal to in excess of 90%, utilizing only a two stage operational procedure. The method in accordance with the invention for producing the substantially carrierless iron catalysts

which may contain small amounts of copper or similar metals as auxiliary components, essentially comprises precipitating a hot solution of the metal nitrate used, while intensively stirring, with a hot caustic soda solution in such manner that the pH value after the precipitation is about 6.8 - 7.2, washing the precipitated mass down to a K_2O calculated content of at the most 0.5 parts by weight of K_2O for every 100 parts by weight of iron content, stirring at first with a small amount of water for the purpose of comminution, thereafter converting into a suspension by the addition of further amounts of water, adding to this suspension amounts of a potassium water glass solution sufficient to yield 20 - 25 parts by weight SiO_2 for every 100 parts by weight of iron contained in said catalyst, thereafter adding nitric acid in amount sufficient to yield for the catalyst mass remaining after filtration a K_2O to SiO_2 ratio of about 1:4 - 1:5, thereafter drying this catalyst mass and immediately molding the same without return of pulverulous components, and finally subjecting the molded catalyst to a reduction with a reducing gas at temperatures of about 200 - 350°C. and preferably 260 - 300°C. using relatively high gas velocities of about 1 - 2 meter per second and carrying the reduction to a point at which the catalyst contains about 30 - 50% of its total iron content in the form of substantially free iron.

When using iron catalysts prepared in accordance with the invention, it is possible to convert water gas with only a two-stage operation to in excess of 90% with a gas load which is 10 - 20 times that of normal. One of the two synthesis stages is operated with straight passage of synthesis gas, while the other is operated with gas recycling, whereby a ratio of gas to recycled gas of from 1:1 to 1:3 is used.

The use of potassium salts of substantially non-volatile acids is important for the impregnation of the catalysts, since the characteristics of the new catalyst in accordance with the invention are not obtainable with alkali hydroxide, carbonate acetate or similar salts. The pH value of 6.8 - 7.2 is critical for the precipitation because the precipitated catalyst mass is only difficultly filterable and washable at pH values which are higher or lower than those given. For the purpose of stirring the press-off filter cake, the amounts of water specified for the comminution and formation of the suspension must be observed, since it is otherwise not possible to obtain the desired impregnation with a sufficient degree of certainty.

When molding the catalyst, it is not possible to resort to a return of pulverulent components, as is, for instance practised in the production of cobalt catalysts, because the catalyst in accordance with the invention would in that case exhibit a decreased activity and an insufficient firmness of grain. Only if the catalyst is molded immediately upon filtration will there be substantial stability of its granular structure and optimum synthesis characteristics.

In the reduction of iron catalyst in accordance with the invention efficient and active catalysts are obtained only when utilizing relatively high gas velocities. When using low gas velocities, such as hitherto practised, iron catalysts of insufficient activity are obtained.

EXAMPLE I

1000 liters of a hot solution containing per liter 40 g. iron in the form of $\text{Fe}(\text{NO}_3)_3$ and 2 g. CU in the form of $\text{Cu}(\text{NO}_3)_2$ were admixed with 1050 liters of a hot solution containing per liter 100 g. Na_2CO_3 while vigorously stirring.

the mass. The stirring of the mix was continued until the split-off carbon dioxide was completely removed for which purpose the mix was maintained at a constant boil.

5 Upon completed precipitation, the mix showed a pH value of about 7.0. The precipitated metal compounds were then separated in a filter press from their solution, and they were immediately thereafter washed with hot condensate water
10 for 30 minutes at a pressure of 3kg/cm^2 in excess of atmospheric for the purpose of removing the alkali to an appreciable extent. When observing the pH value of 7, the alkali content of the filter cake may be lowered without difficulty to a
15 point that the same (calculated as K_2O) is about 0.4 parts by weight of K_2O for each 100 parts by weight of iron. If, on the other hand, the precipitation is effected at an alkaline pH, it was impossible to obtain in spite of an appreciably prolonged washing, a reduction of the
20 alkaline content below about 1.5 - 2 parts by weight of K_2O for each 100 parts by weight of iron.

 The washed filter cake was then stirred to a slurry with little water in a mixer for the purpose of obtaining the best possible comminution
25 of the moist mass. For this purpose, there were added 30 liters of water for every 100 kg of the moist filter cake. The comminuted catalyst mass was thereupon mixed with further 350 liters of
30 water until a substantially uniform suspension of almost silk-like consistency was obtained.

Immediately thereafter, 17 kg potassium water glass solution were added, the same containing about 8.1% K_2O and about 20.5% SiO_2 .

5 The suspension impregnated with the potassium water glass was then neutralized with 2.1 liters of nitric acid (48% HNO_3) for every 100 kg of the moist filter cake, the acid being added with intensive stirring in a thin stream. After the neutralization, the suspended material was
10 filtered from the solution in a filter press. The separated filter cake contained about 100 parts by weight of iron (Fe), 4.6 parts by weight of K_2O , and 23 parts by weight of SiO_2 .

15 The filter cake was then molded without return of pulverulent components into cylindrical particles of about 2 - 4 mm diameter and 3 - 6 mm length, whereby extraordinarily hard and resistant catalyst particles were obtained. These were then reduced at about 280° C. with a hydrogen-nitrogen mixture for
20 about 60 minutes, utilizing a gas velocity of about 1.5 m (linear velocity measured cold) per second. The reduced catalyst thus obtained contained about 42% of the total iron content in the form of free iron.

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

1. Method for the production of iron catalysts for the catalytic carbon monoxide hydrogenation which comprises adding to a solution of iron nitrate conventionally used for the preparation of carbon monoxide hydrogenation catalyst an iron hydroxide precipitant in amount sufficient to obtain a pH end point of from about 6.8 to 7.2 while continuously stirring, separating the precipitate, washing the same to reduce its alkali contents to a maximum of 0.5 parts by weight of K_2O for each 100 parts by weight of iron content in said precipitate, thereafter preparing an aqueous slurry of said precipitate, adding further amounts of water to said slurry to thereby obtain a suspension of said precipitate, adding a potassium water glass solution to said suspension in amount sufficient to yield 20 to 25 parts by weight of SiO_2 for every 100 parts by weight of iron contained in said suspension, thereafter adding nitric acid in amount sufficient to yield for the residue after filtration thereof K_2O to SiO_2 proportion of about 1:4 to 1:5, thereafter drying the filter residue and moulding the same into particles without return of pulverulent components, reducing the moulded particled material with a reducing gas at a velocity of about 1 to 2 meters per second and a temperature of about 200 to 350°C. until said material yields at least 30 to 50% of its iron content in the form of free iron.

2. Method in accordance with Claim 1, in which said precipitant is a hot aqueous solution of an alkali metal carbonate.

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3. Method in accordance with Claim 2 in which said alkali metal precipitant solution is a hot soda solution.

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