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HYDROCARBON SYNTHESIS PROCESS

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This invention relates to the catalytic conver-
sion of carbon oxides with hydrogen to form
valuable synthesis products. More particularly,
this invention is concerned with an improved
method and catalyst permitting a high degree
of flexibility in carrying out this synthesis using
the fluid solids technique, at the same time re-
tarding or preventing catalyst disintegration and
obtaining exceptionally high yields of valuable
liquid products.

The synthetic production of liquid hydro-
carbons from gas mixtures containing various
proportions of carbon monoxide and hydrogen is
already well known, and numerous catalysts,
usually containing an iron group metal, have been
described which are specifically active in promot-
ing the desired reactions at certain preferred
operating conditions. Thus cobalt supported on
kieselguhr is used when relatively low pressures
of 15 to about 75 pounds and low temperatures of
about 375°-425° F. are applied in the manufac-
ture of a substantially saturated hydrocarbon
product while at the higher temperatures
(450°-750° F.) and higher pressures of 5-30 at-
mospheres and higher required for the production
of unsaturated and branch chained products of
high anti-knock value, iron type catalysts are
more suitable.

In both cases the reaction is strongly exo-
thermic and the utility of the catalyst declines
steadily in the course of the reaction, briefly
due to the deposition of non-volatile conversion
products, such as carbon, paraffin wax, and the
like on the catalyst.

The extremely exothermic character and high
temperature sensitivity of the synthesis reactor
and the relatively rapid catalyst deactivation has
led, in recent years, to the application of the so-
called fluid solids technique wherein the synthesis
gas is contacted with a turbulent bed of finely
divided catalyst fluidized by the gaseous re-
actants and products. This technique permits
continuous catalyst replacement and greatly im-
proved heat dissipation and temperature control.

However, the adaptation of the hydrocarbon
synthesis process to the fluid solids technique has
encountered serious difficulties particularly with
respect to catalyst deposits and their detrimental
effects on the fluidization characteristics and
mechanical strength of the catalyst.

As stated above, one of the most important
modifications of the hydrocarbon synthesis re-
action requires the use of iron type catalysts.
These catalysts combine a high synthesizing
activity and selectivity to normally liquid prod-

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ucts with a strong tendency to carbonize during
the synthesis reaction, that is, to form fixed
carbon or coke-like catalyst deposits, probably as
a result of the reaction $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$. These de-
posits cannot be readily removed by conventional
methods of synthesis catalyst regeneration, such
as solvent extraction, reduction, steam treating,
or the like.

These carbon deposits weaken the structure
of the iron catalyst crystal, probably due to
carbide formation, and lead to rapid catalyst dis-
integration, particularly in fluid solids operation,
by shattering the crystal structure. The reduc-
tion of the true density of the catalyst resulting
from its high content of low density carbon,
coupled with the rapid disintegration of the cata-
lyst particles, causes the fluidized catalyst bed
to expand, thereby reducing its catalyst concen-
tration and ultimately resulting in the loss of the
catalyst bed because it becomes impossible to hold
the catalyst in a dense phase at otherwise similar
fluidization conditions. With these changes in
fluid bed characteristics the heat transfer from
and throughout the bed decreases markedly,
favoring further carbonization and accelerating
the deterioration of the fluidity characteristics of
the bed.

Prior to the present invention it has been found
that this disintegration of the catalyst bed due
to carbon formation may be substantially reduced
by supporting the iron catalyst in an inert car-
rier. Thus it has been suggested to use silica gel,
kieselguhr, pumice, carbon and the like. The ad-
vantage of using a carrier support is that carbon
formation only attacks the surface of the sup-
ported catalyst, but will not penetrate the inert
interior or core, thus substantially reducing the
quantity of non-fluidizable material.

In spite of the increased resistance to disinte-
gration due to carbon formation, the use of cata-
lyst supported on carriers has been accompanied
by certain disadvantages. Thus the mechanical
strength of some carriers such as kieselguhr, while
adequate for a fixed bed process, is insufficient to
withstand the attrition effects accompanying the
fluid solids process, and the catalyst support dis-
integrates. Furthermore, due to the dilution
effect of the inert material, catalyst supported on
carriers have not always shown the same selec-
tivity and conversion as the unsupported ma-
terial. Furthermore, certain catalyst carrier ma-
terials have undesirable effects upon the synthe-
sis products.

The present invention overcomes these difficul-
ties and affords various additional advantages as

will be apparent from the description to follow. It is, therefore, the principal object of the invention to provide an improved process for the catalytic synthesis of hydrocarbons from CO and H₂.

Another object of the invention is to provide an improved iron synthesis catalyst supported on a carrier and improved means for preparing the same.

Still another object of the invention is to increase the flexibility and adaptability of the iron type fluid hydrocarbon synthesis process. Other objects and advantages will appear hereinafter.

It has now been found that an excellent disintegration resistant catalyst can be prepared by impregnating Alundum with an iron salt, such as ferric nitrate, and with a suitable alkali metal salt promoter. Not only has the catalyst thus formed considerable mechanical strength but also it has been found to give exceptionally high yields of valuable liquid hydrocarbon synthesis products, and also is found to be exceptionally active in terms of synthesis gas converted.

The use of Alundum as a carrier for an iron synthesis catalyst has the further advantage of having a comparatively low bulk density. The lower bulk density of an Alundum supported iron synthesis catalyst increases substantially the ease of fluidization, decreasing the pressure in the feed gases needed to keep the mass fluidized. Thus Alundum based iron synthesis catalyst has a Le Chatelier density of about 3.95 gms./cc. as compared with a typical iron base catalyst of 4.95. For comparison, silica-magnesia cracking catalyst has a Le Chatelier density of 2.4 and is known to be considerably more readily fluidizable than the more massive unsupported iron synthesis catalyst. Alundum base synthesis catalyst, therefore, approaches cracking catalyst in its adaptability to fluidization. However, while cracking catalyst has a high attrition value, as indicated by the fact that a Roller attrition of a silica-alumina catalyst shows an increase of 3% to 4% in 0-10 micron fractions per hour after the first hour, Alundum base iron synthesis catalyst shows only a 1.23% increase indicating its high mechanical strength. This is close to the value for an unsupported iron catalyst, such as ammonia synthesis catalyst.

To illustrate this desirable property, in the table below is given a typical Roller analysis of an Alundum impregnated iron type hydrocarbon synthesis catalyst.

Particle Diameter	Weight Percent	Time Rate
0-10	10	1.23%
10-20	1	(= Percent 0-10 micron material formed per hour after first hour of Roller attrition).
20-40	1	
40-80	2	
80+	86	

In accordance with the present invention, supported iron type synthesis catalysts of great mechanical strength and highest activity and liquid product selectivity are prepared by impregnating Alundum, which is a product containing from about 75-95% Al₂O₃ and 2-20% silica, with varying minor amounts of oxides of magnesium, calcium, titanium, and iron, and which has been prepared by fusing bauxite or other aluminum oxide ore at a temperature over 2000° F. with silica and with minor quantities of clay and feldspar, and impregnating with an iron salt and a catalyst promoter. Because of the high tem-

perature treatment to which the mixture has been exposed, the surface area is low, and hence the activity of the alumina is destroyed and its deleterious effect upon the synthesis products is prevented.

In a specific example Alundum base synthesis catalyst was prepared as follows:

A sample of Alundum was prepared by fusing pure (99.58%) alumina with silica to give a product analyzing as follows:

	Per cent
Al ₂ O ₃	85.5
SiO ₂	12.1
Fe ₂ O ₃	0.5
MgO	0.2
CaO	0.2
Na ₂ O	0.4
K ₂ O	0.3
TiO ₂	0.8

150 grams of the above material was impregnated with 191 grams of Fe(NO₃)₃ · 9H₂O in 50 cc. H₂O. The mass was dried in a Freas oven. Thereupon the mass was heated in a muffle furnace for 2 hours at 800° F. to decompose the nitrates. Thereupon the product was impregnated with 3.85 grams of K₂CO₃ dissolved in 50 cc. water and again dried in a Freas oven. The resulting catalyst material was analyzed and found to contain 11.9% iron and 1.6% potassium promoter as K₂O.

Catalysts of different origin and composition, both supported and unsupported were tested in fixed bed operation at the conditions and with the results tabulated in the example below.

Example

[All runs carried out at 250 p. s. i. g. and 600° F. except*.]

Catalyst Composition	Run, Hrs.	Feed Gas Ratio, H ₂ /CO	CO Conversion Output	cc. C ₄ + / m. ³ H ₂ + CO Consumed
1. Alundum base	14-85	1.1/1	97	228
	86-109	1.1/1	97	235
	134-157	2/1	97	219
	158-181	2/1	97	218
	182-255	2/1	97	207
2. Ammonia Synthesis Catalyst, Unsupported *(650° F.)	15-86	2/1	97	156
	135-153	2/1	97	160
	519-590	2/1	96	153
3. Ammonia Synthesis Catalyst Supported on Active alumina.	53-100	2.1/1	84	160
	221-263	2.1/1	78	130
	339-436	2.1/1	86	138

The standard ammonia synthesis catalyst in the above example was a reduced fused magnetite containing about 1.2% K₂O and about 2.5% alumina.

The supported ammonia synthesis catalyst was prepared by precipitating Al(OH)₃ from an aqueous solution of Al(NO₃)₃ with ammonia, washing, and mulling the wet filter cake with ammonia synthesis catalyst and drying.

In the above example, the superiority of the Alundum based catalyst over the standard ammonia synthesis catalyst is readily apparent. In hydrocarbon synthesis practice, yields over 180 cc. of liquid product (C₄+) per cubic meter of CO+H₂ consumed are considered very good, and yields of 200 cc. excellent. The exceptionally high yields obtained by the Alundum based catalyst, and its versatility in giving high yields both with 2/1 and 1/1 gas make it an outstanding catalyst.

The ammonia synthesis catalyst supported on alumina, however, gave considerably poorer results. This may be due in part to the activation

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of alumina which occurs under the conditions of synthesis temperature and pressure. With increased surface area of the alumina carrier, the cracking tendencies of the latter are enhanced, resulting in higher quantities of gases and lower yields of desired liquid product.

The catalyst of the present invention affords the greatest advantages, because of its attrition resistance as well as its resistance to carbon disintegration, in connection with the dense phase fluid type operation. Therefore, the preferred catalyst of the invention essentially consists of particles of fluidizable size of suitably promoted iron catalyst supported on an Alundum carrier, the support preferably carrying about 3% to 35% synthesis catalyst as iron. Particle sizes within the range of 20-200 microns, preferably 50-180 microns are suitable for this purpose.

The invention admits of numerous modifications apparent to those skilled in the art. Thus it may be desirable to use other means than impregnation to put the catalyst in the carrier. Other iron salts that may be used are, for example, $Fe_2(C_2O_4)_3$ and $Fe(CHO_2)_3$. The preferred amount of iron in the carrier is about 5.0 to 15.0%, though higher amounts may be used. The K_2CO_3 promoter content is preferably 0.2 to 2.0% calculated as K_2O , but other alkali metal salt promoters, such as Na_2CO_3 , KF , KOH , etc. may be employed.

While the foregoing description and exemplary

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operations have served to illustrate specific embodiments of the invention, they are not intended to limit its scope. Other modifications may appear to those skilled in the art without departing from the spirit of the invention.

What is claimed is:

In the catalytic synthesis of normally liquid hydrocarbons from CO and H_2 in the presence of an iron-type catalyst, the improvement which comprises contacting said CO and H_2 at synthesis conditions with a catalyst prepared by impregnating an Alundum carrier consisting of about 85% Al_2O_3 and 12% SiO_2 with an iron salt to give a product containing about 5 to 15% iron and incorporating into the product a minor proportion of an alkali metal compound promoter.

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