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## HYDROGENATION OF CARBON MONOXIDE

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The present invention relates to improvements  
in carrying out reactions of carbon monoxide with  
hydrogen, in particular to the conversion of these  
gases into gaseous, liquid and/or solid hydrocar-  
bons or their derivatives containing oxygen.

It has already been proposed to use catalysts  
comprising more than one substance, the main  
constituent being metals of the 8th group of the  
periodic system in the said reactions of carbon  
monoxide with hydrogen for the preparation of  
gaseous, liquid and/or solid hydrocarbons (the  
gaseous hydrocarbons containing more than one  
carbon atom in the molecule) or their derivatives  
containing oxygen. Hitherto, such catalysts  
have usually been prepared by bringing soluble  
compounds containing the single components  
into solution together and then subjecting them  
in this solution to a common further treatment,  
for example by precipitating the components to-  
gether from the solution, drying and reducing, or  
evaporating the solution and then subjecting the  
residue to a decomposing thermal treatment.

We have now found that catalysts of especially  
good activity for the said reaction are obtained  
by precipitating from solutions or suspensions of  
compounds of the metals of the iron group the  
said metals in the form of their difficultly soluble  
or insoluble compounds, adding the further com-  
ponents to the precipitated compounds and then  
subjecting the resulting mixture to a thermal  
treatment which is best effected with reducing  
gases. The procedure may also be that to the  
precipitated compound of a metal of the iron  
group there is added the solution of a compound  
of another metal, the latter then being precipi-  
tated in the presence of the first compound. This  
modification of the preparation according to the  
present invention is particularly advantageous.  
It is likewise advantageous to add the compound  
of another metal to the precipitated compound  
of the metal of the iron group in the form of a  
fresh voluminous precipitate which is another  
form of a dispersion of the added metal com-  
pound with water. Probably the good effect is  
due to the fine distribution of the added metal  
compound on the surface of the iron metal which  
is attained by the addition of the said metal  
compound while dispersed with water.

Of the metals of the iron group, iron itself is  
of special advantage, but also nickel and cobalt  
may be employed. It is precipitated, as are the  
other iron group metals, preferably in the form  
of a compound containing oxygen which is reducible  
to metal with hydrogen, as for example as the  
hydroxide, carbonate, basic acetate or oxalate.

As further components to be added to the afore-  
said compounds of the iron group metals may be  
mentioned for example compounds of aluminum,  
beryllium, manganese, zinc, thorium, cerium, zir-  
conium and other metals of the rare earths, in  
particular metals forming oxides which are not  
reducible to metal with hydrogen at temperatures  
up to 900° C., and they are preferably employed in  
the form of compounds which by heating are de-  
composed with the formation of the oxide, for  
example the nitrates, carbonates, hydroxides or  
salts of organic acids. These further compounds  
may be added in such amounts that the metals  
building them up are present in the mixture in  
amounts up to 30 parts by weight, preferably  
from 0.1 part or still less up to 15 or 20 parts, for  
each 100 parts of the metal from the iron group.

Compounds of the said metals obtained by pre-  
cipitation methods, in particular the hydroxides,  
as for example aluminum hydroxide, may, how-  
ever, be used with equally good results. The salts  
of organic acids, as for example aluminum ace-  
tate, aluminum oxalate and the like have also  
proved to be suitable additions. Two or more of  
the said components may also be added to the  
catalyst. Thus for example good yields are ob-  
tained with catalysts which have been prepared  
by the addition of aluminum hydroxide and  
manganese hydroxide to precipitated iron hy-  
droxide.

As a third or further component there may also  
be used a compound of a metal which forms a  
readily reducible oxide. Thus for example cata-  
lysts which contain not only aluminum nitrate,  
but also copper nitrate as a second additional  
substance to precipitated iron hydroxide, also  
give good yields.

The catalysts provided with the additions are  
then subjected to a thermal treatment, preferably  
in the presence of reducing gases, as for example  
hydrogen, gases containing hydrogen or carbon  
monoxide. This treatment is preferably carried  
out at high temperatures ranging between 500°  
and 1100° C., as for example at 800° C., whereby  
at least a partial sintering of the catalyst takes  
place. The thermal treatment may also be car-  
ried out in two or more stages, for example by  
first heating the catalysts in the presence of non-  
reducing gases, as for example nitrogen or air,  
and then with reducing gases.

The thermal treatment in one or more stages  
may take place at atmospheric pressure or at  
pressures of any value, as for example at 2, 5, 10,  
50, 100 atmospheres or more. In some cases,  
when working in two or more stages, it is also

advantageous to use different pressures in the single stages.

The reaction with carbon monoxide and hydrogen is carried out at temperatures above 150°, preferably between 200° and 450° C. The proportions of carbon monoxide and hydrogen may be for example 1:1 (calculated by volume), but this ratio may be varied in favor of hydrogen or carbon monoxide. The hydrocarbon synthesis for which the catalysts prepared according to this invention are of particular advantage may be carried out at any desired pressure. It is preferable, however, to use increased pressure, as for example 5, 10, 20, 50, 100 atmospheres or more.

The following examples will further illustrate the nature of this invention but the invention is not restricted to these examples. The parts are by weight.

#### Example 1

Iron hydroxide is precipitated and filtered off. A suspension of precipitated aluminum hydroxide is added to the still moist iron hydroxide, the amounts being such that there are 5 per cent of aluminum oxide with respect to metallic iron. The mixture of the hydroxides is then intimately stirred and dried in a drying cabinet and reduced in a stream of hydrogen at 850° C.

If a mixture of equal parts of carbon monoxide and hydrogen be led over the said catalyst at a pressure of 15 atmospheres and at a temperature of 300° C., there are formed, in addition to small amounts of products containing oxygen, mainly liquid hydrocarbons and small amounts of gaseous and solid hydrocarbons. The amount of liquid and solid products obtained per day is equal to the volume of the catalyst used.

If on the other hand the iron hydroxide is precipitated together with the aluminum hydroxide, filtered off and reduced, the yield of liquid and solid products under the same reaction conditions is considerably less. It amounts to only about one quarter of the volume of the catalyst used per day.

#### Example 2

Precipitated iron hydroxide is made into a paste with an aqueous solution of aluminum nitrate. The aluminum nitrate is added in such an amount that there are 10 per cent of aluminum oxide with respect to metallic iron. The paste is dried in a drying cabinet and treated at 800° C. with hydrogen.

If a mixture of carbon monoxide and hydrogen be led over the catalyst thus prepared under the reaction conditions specified in Example 1, there are obtained in the course of a day about one and a half times the catalyst volume of liquid and solid products.

What we claim is:

1. A process for the thermal conversion of carbon monoxide with hydrogen into organic compounds selected from the group consisting of liquid and solid hydrocarbons and gaseous hydrocarbons containing more than one carbon atom in the molecule which comprises heating the said carbon monoxide and hydrogen in the presence of a catalyst which has been prepared by precipitating from a solution of an iron group metal compound such difficultly soluble or insoluble compound of the said metal as is easily reducible to the metal by heating in the presence of hydrogen, adding to the precipitated compound such compound of another metal as by heating yields an oxide not reducible to metal by hydrogen below 900° C., and subsequently heating the resulting mixture in the presence of a gas having a reducing action to a temperature above 500° C. for a period of time sufficient to effect sintering.
2. In the process as claimed in claim 1, operating in the presence of a catalyst prepared by adding to the precipitated iron group metal compound the other compound in the form of a dispersion with water.
3. In the process as claimed in claim 1, operating in the presence of a catalyst prepared by adding a compound of a metal selected from the group consisting of aluminum, beryllium, manganese, zinc and metals of the rare earths to a precipitated compound of iron which is easily reducible by hydrogen.
4. In the process as claimed in claim 1, operating in the presence of a catalyst prepared by adding precipitated aluminum hydroxide to a precipitated compound of iron which is easily reducible by hydrogen.
5. In the process as claimed in claim 1, operating in the presence of a catalyst prepared by adding a solution of aluminum nitrate to a precipitated compound of iron which is easily reducible by hydrogen, drying the resulting mass and subsequently heating it to a sufficiently high temperature to effect at least partial sintering of the catalyst in the presence of a gas having a reducing action.
6. In the process as claimed in claim 1, operating in the presence of a catalyst prepared by adding a solution of aluminum nitrate to a precipitated compound of iron which is easily reducible by hydrogen, precipitating aluminum hydroxide from the said solution and subsequently heating the mixture of precipitates to a sufficiently high temperature to effect at least partial sintering of the catalyst in the presence of a gas having a reducing action.

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