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PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Process for the Catalytic Production of Methanol.

We, COMMERCIAL SOLVENTS CORPORATION, a corporation organized and existing under the laws of the State of Maryland, United States of America, located at Terre Haute, County of Vigo, State of Indiana, United States of America, (Assignees of JOHN CAULFIELD WOODRUFF, of 1526, South Sixth Street, Terre Haute, Indiana, United States of America, GROVER BLOOMFIELD, of 1306, South Center Street, Terre Haute, Indiana, United States of America, and WILLIAM JAMES BANNISTER, of 1430½, South Center Street, Terre Haute, Indiana, United States of America, all citizens of the United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of methanol by the high pressure catalytic combination of oxides of carbon with hydrogen, and pertains more directly to the preparation of improved catalysts and their use in the process.

Methanol may be produced by combining oxides of carbon with hydrogen in the presence of a suitable catalyst at elevated temperature and pressure. Carbon monoxide, carbon dioxide, and mixtures of the two oxides may be employed, these substances reacting with hydrogen according to the following equations:—

I. Carbon monoxide – $CO + 2H_2 = CH_3OH$

II. Carbon dioxide – $CO_2 + 3H_2 = CH_3OH + H_2O$

It is observed that when carbon dioxide is the oxide employed, one molecule of water is formed for every molecule of methanol produced. On the other hand when pure carbon monoxide is used, theoretically there is nothing produced by the reaction but methanol. Actually in practice pure carbon monoxide and pure carbon dioxide are both difficult to obtain economically, so that the methanol synthesis is frequently carried out by reacting a mixture of carbon monoxide and carbon dioxide with hydrogen.

The production of methanol by the interaction of hydrogen and carbon oxides is essentially a hydrogenating reaction effected by hydrogenating catalysts. While the methanol reaction is ordinarily represented according to equations I and II above, it is probable that there is an intermediate reaction and that this reaction may involve the production of formaldehyde which is afterwards further hydrogenated to methanol, thus:—

III. $CO + H_2 = CH_2O + H_2 = CH_3OH$

In the case of carbon dioxide, the first reaction occurring is probably the reduction of that material to carbon monoxide, and Equation II may thus be expanded as follows:—

IV. $CO_2 + H_2 = H_2O + CO$

$CO + H_2 = CH_2O + H_2 = CH_3OH$

Under certain conditions no methanol is produced by the high pressure catalytic reaction of hydrogen and carbon monoxide—only methane being formed. This reaction is illustrated by the following equation:—

V. $CO + 3H_2 = CH_4 + H_2O$.

It is, of course, certain that Equation V represents a summation of several intermediate reactions. It represents the complete hydrogenation of carbon monoxide.

A possible course of reaction is indicated below.

VI. $CO + H_2 = CH_2O$

$CH_2O + H_2 = CH_3OH$

$CH_3OH + H_2 = CH_4 + H_2O$

In addition to the methane reaction there are other side-reactions which sometimes occur in which there are produced esters, aldehydes, organic acids, ketones, and hydrocarbons other than methane; these reactions occurring as the result of the polymerization or condensation of methanol or its decomposition products.

When a gas mixture comprising carbon oxides mixed with an excess of hydrogen over the amount theoretically required to produce methanol is passed over a catalytic substance consisting of metals or their oxides at a pressure above 60 atmospheres and at a temperature above 250° C. there is nearly always produced some reaction between the gaseous components. The extent of this reaction depends to some degree on space velocity, temperature, and pressure, but the fact remains

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that under the conditions outlined carbon oxides and hydrogen react to some extent in all cases.

The substances formed by such a process depend, both as to identity and as to amount, almost entirely on the nature and activity of the catalytic substance present. The methanol catalysts mentioned in prior patents and literature are combinations of metals or their oxides which substances normally exert a hydrogenating catalytic effect on gas reactions.

The literature on the high pressure catalytic process for synthesizing methanol states that the presence of nickel or any of its compounds in a catalyst destroys or poisons the catalyst and tends to inhibit methanol formation. While nickel obtained by a reduction process is an excellent hydrogenating catalyst for many reactions, it has been reported to react with carbon monoxide, and with mixtures of hydrogen and the carbon oxides (i.e. carbon monoxide and/or carbon dioxide) used in the methanol reaction, forming a volatile carbonyl compound which, it has been stated, inhibits the methanol reaction. The normal effect of the presence of nickel in a methanol catalyst according to present theories is to cause the reaction of hydrogen and carbon oxides to produce mainly methane and water.

We are aware that it has been proposed to prepare nickel catalysts for reduction processes by the reduction of a nickel compound in the presence of a carrier by the action of hydrogen at temperatures of 400° C. or higher. A temperature of about 550° C. has also been proposed for the reduction of nickel compounds with hydrogen and for a subsequent glowing of the product in a stream of carbon dioxide, moreover nickel has been reduced with carbon or a carbon-containing compound at 550° to 650° C. in a non-oxidising atmosphere, the catalyst produced being used in the hydrogenation of fatty oils.

A further known method consists in the preparation of nickel catalysts for use in the production of methanol wherein the nickel is in the state of an alloy, with the metal element of a difficultly reducible metal oxide, or compounded with the metalloid element of a difficultly reducible non-metal oxide, the nickel being saturated or even supersaturated with the dissolved or compounded element. In this case the nickel compound is reduced in the presence of a difficultly reducible oxide at a temperature of not more than 400° C. and the ultimate catalyst contains nickel in chemical combination or in the form of an alloy or a solid solution.

In the methanol art it has never been thought possible hitherto to use a nickel catalyst in which the nickel is in a free condition and uncontaminated with other compounds or metals since the activity of this catalyst in the form as known hitherto is so great as to decompose any methanol produced when such a catalyst is employed.

According to the present invention, however, an improved process of producing methanol is disclosed, in which hydrogen and carbon monoxide and/or carbon dioxide are passed under pressure at an elevated temperature over a catalyst consisting of nickel, and this invention is characterised by the fact that the nickel employed has been prepared by reducing a nickel compound by the action of hydrogen at a temperature of from 300° to 950° C. Preferably a reduction temperature of from 500° to 600° C. is used and it is sometimes advantageous to permit the nickel thus produced to cool in the atmosphere of hydrogen prior to use.

It has been discovered that a nickel catalyst of this type is suitable for use in the high-pressure synthesis of methanol, all of the prior art literature not withstanding. The lack of success of prior efforts to employ nickel catalysts in the synthetic methanol reaction is attributed to the character and to the degree of catalytic activity of the nickel catalyst employed. According to our own experiments, ordinary nickel catalysts such as have been employed in other similar chemical processes are not suitable for synthetic methanol production. It has been discovered, however, that nickel, prepared by the treatment with hydrogen at elevated temperature of reducible compounds of nickel such as the hydrate, the oxide, the nitrate, or various organic salts such as the oxalate or tartrate, may form a very valuable catalyst for synthetic methanol production.

In prior attempts to adapt nickel catalysts to synthetic methanol production a catalyst of high activity has apparently been employed and the result attained has merely been the complete hydrogenation of carbon monoxide to methane, as was indicated in Equations V and VI. The nickel catalysts which were found valueless in prior art tests were composed of nickel or nickel oxide in admixture with an inert support or in admixture with another catalytic oxide. In case the catalyst initially contained nickel oxide, it would, of course, be largely reduced to metallic nickel, either prior to or during use. It is a fact well-established in the catalytic hydrogenation art that nickel obtained by a reduction process while in admixture with an inert supporting mass is a more active catalyst than is the nickel obtained from the identical nickel compound when reduced at the same temperature in the absence of a supporting medium. It is also well known that a reduction temperature above 300° C., all other things being equal, produces a less active nickel catalyst than does a lower temperature. It has been found, however, that a granular nickel catalyst prepared by the reduction of nickel compound, per se, may satisfactorily serve as a methanol catalyst, provided the proper degree of activity is imparted during the reduction.

Nickel obtained by a reduction process at temperatures in excess of 950° C. has little or no catalytic effect in the synthetic methanol reaction. This fact is attributed to the character of the nickel; obtained by reduction at so high a temperature it is too inactive a catalyst. Nickel obtained by a reduction process at temperatures below 300° C. is so active a catalyst that its effect in the synthetic methanol reaction is to completely hydrogenate carbon monoxide and thus to produce only methane. It has been discovered that nickel catalysts produced by the reduction of nickel compounds with hydrogen within a temperature range of 300—950° C. may be employed in the synthetic methanol reaction. It has been further discovered that nickel obtained by reduction of nickel compounds with hydrogen within a temperature range of 500—600° C. is the best synthetic methanol catalyst.

In the tabulation below the results attained in the synthetic methanol process are shown with the improved nickel catalysts forming the subject matter of this invention. The process was carried out by passing a mixture of from 84 to 82% of hydrogen and 16 to 18% of carbon monoxide through 10 c.c. of granular nickel catalyst under the pressures and at the temperatures indicated, the methanol being recovered by cooling the reacted gases and condensing under pressure. The per cent. methanol in the condensate is reported and it should be understood that the residual per cent. of condensate in all cases was water.

Production of catalyst by reduction. °C	Reaction temp. °C.	Reaction pressure (lbs. per sq. inch.)	Space velocity of gases	c.c. condensate per hour	% methanol	% carbon monoxide in gas
300	400	3000	10,000	1.3	51.0	16.5
300	400	3000	20,000	2.2	47.5	16.5
300	400	3000	40,000	3.4	43.7	16.5
500	400	3000	20,000	4	20	16.0
500	420	3000	40,000	3.4	46.5	17.0
550	400	3000	5,000	1.3	78	17.0
550	400	3000	3,500	1.1	82	17.0
550	400	3000	10,000	2.0	62.9	17.0
550	400	3000	20,000	3.5	53.9	17.0
550	400	3000	40,000	3.4	49.5	17.0
550	400	3000	60,000	6.0	50.2	17.0
600	380	2000	75,000	4.7	45.8	10*
600	435	2000	75,000	2.7	49	16.6
950	400	3300	20,000	1.8	44.3	16.9
950	400	3300	40,000	2.5	41.6	16.9
950	430	3000	35,000	2.6	41.0	16.0

*Carbon dioxide replaced carbon monoxide in this test.

The space velocity given in column four above is the number of volumes of gas, measured at standard conditions, passed over one volume of catalyst in one hour.

For the purpose of producing the improved catalysts, as a base material any easily-reducible compound of nickel may be employed, for example the hydrate, oxide, nitrate, tartrate, or oxalate. The reduction may be carried out in the ordinary manner, known to those skilled in the art, which consists in heating granules of the nickel compound to the proper temperature in a current of hydrogen. The precise time required for reduction depends on the area of material exposed and the space velocity of the hydrogen. When reduction is completed it is preferable, though not necessary, that the produced catalyst be allowed to cool down to room temperature in a hydrogen atmosphere. Once prepared, the catalyst is not damaged by exposure to air.

If desired the reduction may be accomplished in the synthetic methanol apparatus immediately prior to use.

When granules of a nickel compound are reduced with hydrogen within the temperature range 300—950° C. the nickel catalyst so produced is suitable for methanol production, as was shown in the above tabulation. Nickel thus produced below 300° C. retains a powdery character and no particle fusion is noted. The catalytic activity of such material is so great that complete hydrogenation of carbon oxides is attained. Nickel thus produced within the temperature range 300—950° C. is apparently in a state of incipient fusion such that it has just enough catalytic activity to carry the hydrogenation of carbon monoxide to the methanol stage. Nickel obtained by reducing a nickel compound with hydrogen above 950° C. is according to our belief so completely fused as to destroy the catalytic activity in methanol work.

Granules of nickel compound suitable for reduction may be prepared by moistening the powdered or crystalline compound with water, compressing the moist mass into tablet form, and permitting it to dry slowly. In place of pure water, a dilute aqueous solution of an agglutinating substance such as dextrine may be employed, and better granules thus obtained.

Nickel hydrate in pure form and in dense granules highly suitable for reduction and subsequent use as a catalyst may be prepared in the following manner:—

A solution of nickel nitrate $Ni(NO_3)_2.6H_2O$ or similar soluble nickel salt is made up in distilled water to a concentration of about 1%. This solution is heated to 95—100° C. and is then treated with sufficient ammonium hydroxide to just render it alkaline, as indicated by "brilliant yellow" indicator paper.

The precipitate thus formed is allowed to settle and the supernatant liquor is removed by syphoning or decantation. The precipitated nickel hydroxide is separated in any convenient manner, for example by centrifuging, and is washed with about five times its volume of distilled water. The precipitate is again separated, and on account of its voluminous character the final separation from the wash water is most conveniently done with a centrifuge. The moist precipitate is then spread out on plates in layers about 1 cm. in thickness and dried at 100—105° C. for about 10—15 hours. The precipitate forms hard dense cakes during the drying period, and is subsequently broken up into granules of a size suitable for catalytic use.

It is understood, however, that the specific example of the method of preparing nickel hydrate for reduction and subsequent use as a methanol catalyst is illustrative merely. Other nickel compounds may be used as the basis of a nickel catalyst as was disclosed in a prior section of this Specification.

While in the above tabulation of the results obtained in the production of synthetic methanol with the improved nickel catalysts, the reaction temperatures employed vary from 380—430° C., it should be understood that these catalysts are operative throughout the entire operative range of reaction temperature for synthetic methanol production—that is 250—450° C.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. An improved process of producing methanol which consists in passing a mixture of hydrogen and carbon monoxide and/or carbon dioxide under pressure at an elevated temperature over a catalyst consisting of nickel characterised in this that the nickel catalyst has been formed by the reduction of a nickel compound with hydrogen at a temperature of from 300° to 950° C.

2. An improved process of producing methanol as claimed in Claim 1 wherein the catalyst employed has been reduced at a temperature of from 500° to 600° C.

3. An improved process of producing methanol as claimed in Claims 1 and 2, wherein the nickel catalyst has been permitted to cool in an atmosphere of hydrogen prior to its use.

4. The improved process of producing methanol substantially as hereinbefore described.

Dated this 28th day of March, 1927.
MARKS & CLERK.

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