PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to Catalysts for Gas Reactions

We, NORMAN BOOTH, LESLIE JOHN JOLLEY and JOHN ARTHUR TEBBOTH, all British subjects, and all of the Fuel Research Station, River Way, Blackwall Lane, East Greenwich, London, S.E.10, do hereby declare the nature of this invention to be as follows:—

This application relates to catalysts for gas reactions and especially those reactions involving carbon monoxide, hydrogen, carbon dioxide, steam and aliphatic hydrocarbons. These reactions include the synthesis of hydrocarbons and the water gas shift reaction. In particular the application relates to catalysts for the synthesis of methane.

The synthesis of methane from gases containing carbon monoxide and hydrogen proceeds by one or both of the reactions:—

$$3H_2 + CO = CH_4 + H_2O$$
$$2H_2 + 2CO = CH_4 + CO_2.$$

At the same time there is a tendency for carbon to be deposited by the side reaction

$$2CO = CO_2 + C$$

Suitable catalysts for accelerating the methane forming reactions consist of nickel or cobalt supported on kieselguhr, and promoted by thoria and/or magnesia. Using catalysts of this type almost complete conversion of the carbon monoxide to methane can be effected at temperatures of 300—400° C. and gas rates as high as 4000 volumes per volume of catalyst space per hour, or even higher.

The proportion of the carbon monoxide which decomposes to give carbon is relatively small, i.e. less than one per cent. The result of continued deposition of this carbon however is to obstruct the passage of the gas, and ultimately it becomes impossible to pass gas through the catalyst vessel at the desired rate without an excessive pressure drop. With gases of low hydrogen to carbon monoxide ratio, such as blue water gas or modified blue water gas, the blockage of the catalyst tubes may occur long before the end of the useful life of the catalyst. If a gas of higher hydrogen to carbon monoxide ratio is used, a longer time elapses before blockage occurs.

According to the present invention we incorporate a small amount of phosphorus preferably in combined form in the catalyst. We have found that the rate of deposition of carbon is thereby reduced considerably. The phosphorus may be added in the form of orthophosphate, pyrophosphate or metaphosphate, but metaphosphate is preferred since the resulting catalyst has a longer useful life. The following example illustrates one way in which the present invention may be applied.

A catalyst consisting of nickel, thoria and kieselguhr in the proportions 100:22:100 was prepared in the following way. Nickel and thorium nitrates in the correct proportions were made into a solution and potassium carbonate solution was added with constant stirring. When about four fifths of the amount of carbonate required to precipitate all the nickel and thorium had been added, a suspension of kieselguhr in water was added, and then the remainder of the potassium carbonate solution. The precipitate was filtered, washed, dried, crushed, sized and finally reduced in hydrogen at 400° C.

Further batches of catalyst were made in the same manner, except that a small amount of phosphorus in the form of orthophosphate was added to the potassium carbonate solution prior to use. These catalysts were used in standard experiments in which a water/gas or hydrogen to carbon monoxide ratio of 1.5 to 1 was passed over at a temperature of 350° C. and a space velocity of 3700 volumes of gas per volume of catalyst per hour. The carbon deposited was determined by burning it off and measuring the carbon dioxide formed. The effect of additions of varying amounts of phosphorus in reducing the carbon deposition is shown in the following table.

Per cent of phosphorus in potassium carbonate.	Per cent of ingoing carbon deposited.
0	0.4770
0.25	0.3610
0.5	0.1920
0.75	0.0464
1.0	0.0237
1.25	0.0192

[*Price* 1/-]

Dated the 30th day of November, 1943.

H. K. WARR-LANGTON,
Agent for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to Catalysts for Gas Reactions

We, Norman Booth, Leslie John Jolley and John Arthur Tebboth, all British subjects, and all of the Fuel Research Station, River Way, Blackwall Lane, East Greenwich, London, S.E.10, 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 gas reactions catalyzed by promoted nickel catalysts and involving conversion of carbon monoxide into other products, such as conversion of carbon monoxide with steam to produce hydrogen and carbon dioxide, hereinafter referred to as the water gas shift reaction, and, particularly, the synthesis of methane.

The synthesis of methane from gases containing carbon monoxide and hydrogen proceeds by one or both of the reactions.

$$3H_2 + CO = CH_4 + H_2O$$
$$2H_2 + 2CO = CH_4 + CO_2.$$

At the same time there is a tendency for carbon to be deposited by the side reaction.

$$2CO = CO_2 + C.$$

A suitable catalyst for accelerating the methane forming reactions consist of nickel intimately mixed with a support such as kieselguhr, and promoted by the incorporation, as a minor ingredient, of one or more difficultly reducible metallic oxides such as thoria and/or magnesia. Using a catalyst of this type almost complete conversion of the carbon monoxide to methane can be effected at temperatures of 300—400° C. and gas rates as high as 4000 volumes per volume of catalyst space per hour, or even higher. A catalyst of this type is also suitable for other gas reactions involving carbon monoxide, such as the water gas shift reaction.

The proportion of the carbon monoxide which decomposes to give carbon is relatively small, i.e. less than one per cent. The result of continued deposition of this carbon however is to obstruct the passage of the gas, and ultimately it becomes impossible to pass gas through the catalyst vessel at the desired rate without an excessive pressure drop. With gases of low hydrogen to carbon monoxide ratio, such as blue water gas or modified blue water gas, the blockage of the catalyst tubes may occur long before the end of the useful life of catalyst. If a gas of higher hydrogen to carbon monoxide ratio is used, a longer time elapses before blockage occurs.

According to the present invention we carry out the reaction with a catalyst which incorporates a small amount of phosphorus. We have found that the rate of deposition of carbon is thereby reduced considerably. The phosphorus may be added in the form of orthophosphate, pyrophosphate or metaphosphate but metaphosphate is preferred since the resulting catalyst has a longer useful life.

The catalyst used in the invention may conveniently be prepared by depositing the nickel and the promoter from a solution of soluble salts thereof, for example the nitrates, by means of a solution of alkali carbonate also containing a small proportion of phosphate. The support may be introduced during the addition of the carbonate solution.

The following examples illustrate how the present invention can be applied.

Example 1.

A catalyst consisting of nickel, thoria and kieselguhr in the proportions 100:22:100 was prepared in the following way. Nickel and thorium nitrates in the correct proportions were made into a solution and potassium carbonate solution was added with constant stirring. When about four fifths of the amount of carbonate required to precipitate all the nickel and thorium had been added, a suspension of kieselguhr in water was added, and then the remainder of the potassium carbonate solution. The precipitate was filtered, washed, dried, crushed, sized and finally reduced in hydrogen at 400° C.

Further batches of catalyst were made in the same manner, except that a small amount of phosphorus in the form of potassium orthophosphate was added to the potassium carbonate solution prior to use. These catalysts were used in standard experiments in which a water gas of hydrogen to carbon monoxide ratio of 1.5 to 1 was passed over at a temperature of 350° C. and a space velocity of 3700 volumes of gas per volume of catalyst per hour. The carbon deposited was determined by burning it off and measuring the carbon dioxide formed. The effect of additions of varying amounts of phosphorus in reducing the carbon deposition is shown in the following table.

Per cent of phosphorus in potassium carbonate.	Per cent of ingoing carbon deposited.
0	0.4770
0.25	0.8610
0.5	0.1920
0.75	0.0464
1.0	0.0237
1.25	0.0192

EXAMPLE 2.

The catalyst was prepared as in Example 1 but incorporating sodium metaphosphate. The effect is shown in the following table.

Per cent of phosphorus in potassium carbonate.	Per cent of ingoing carbon deposited.
0	0.4770
0.25	0.2348
0.5	0.0188
0.6	0.0431

EXAMPLE 3.

The catalyst was prepared as in Example 1 but using potassium pyrophosphate. The effect is shown in the following table.

Per cent of phosphorus in potassium carbonate.	Per cent of ingoing carbon deposited.
0	0.4770
0.5	0.1550
0.8	0.0506

A catalyst comprising nickel, thoria, magnesia and kieselguhr in the proportions 100:6:12:100 was prepared as in Example 1 except that the appropriate amount of magnesia was mixed with the suspension of kieselguhr in water and that the precipitation was carried out with an equivalent amount of sodium carbonate in solution, in which sodium metaphosphate was incorporated. The effect of the phosphorus is shown in the following table.

Per cent of phosphorus in potassium carbonate.	Per cent of ingoing carbon deposited.
0	0.9718
0.5	0.0882
0.8	0.0186
1.0	0.0383

It has already been proposed to convert oxygen-containing organic compounds of a higher order than methanol obtainable by the catalytic hydrogenation of oxides of carbon into colourless products consisting substantially of higher alcohols, by treating such products while in the vapour state with hydrogen free from oxides of carbon at an elevated temperature in the presence of a hydroenating catalyst consisting of granulated pumice stone, nickel carbonate and aluminium phosphate bound together by means of sodium silicate and water, and also containing thoria, tungsten oxide or other like activating agents.

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. A process wherein a gas reaction involving the conversion of carbon monoxide into other products is catalyzed by a catalyst comprising nickel intimately mixed with a support and promoted by the incorporation of one or more difficultly reducible metallic oxides as minor ingredients, in which the catalyst also incorporates a small proportion of phosphorus.

2. A process according to Claim 1 in which the catalyst incorporates a phosphate.

3. A process according to Claim 2 in which the phosphate is a metaphosphate.

4. A catalytic water gas shift process according to Claim 1, 2 or 3.

5. A catalytic methane synthesis according to Claim 1, 2 or 3.

6. A method of preparing the catalyst used in the process claimed in any preceding Claim in which the nickel and the promoter are deposited from a solution of soluble salts thereof by means of a solution of alkali carbonate also containing a small proportion of phosphate.

7. The product when prepared by the process claimed in any of Claims 1 to 5.

Dated this 1st day of January, 1945.

H. K. WARR-LANGTON,
Agent for the Applicants.

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