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(54) PROCESS FOR REACTING OXIDES OF CARBON WITH HYDROGEN TO GIVE METHANE

(71) We, RHEINISCHE BRAUNKOHLENWERKE AG, a German body corporate of, Konrad-Adenauer-Ufer 55, 5000 Koln 1, Germany and FRIEDRICH UHDE GMBH, a German body corporate of, Deggingstr. 10, 4600 Dortmund, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the reaction of carbon oxides, in particular carbon monoxide, and hydrogen to give methane.

The hydrogenation of oxides of carbon to give methane, in the presence of catalysts which contain metals of the eighth group of the Periodic Table, in particular nickel, is known. It has been proposed to operate the process with low CO contents in the feed gas, for example up to 4% by volume (see, for example DOS 2,201,278), or with a large excess of hydrogen, in order to avoid, during the strongly exothermic reaction which takes place, the formation of free carbon, which is favoured as the CO concentration in the reaction mixture increases. Thus, for example, it has been stated that a ratio of H_2:CO of at least 5 is desirable. Hydrogen or a hydrogen-rich gas was passed through a series of reactors filled with a catalyst containing nickel and sufficient CO or CO-rich gas, for example water gas, was added to the hydrogen-rich gas before each reaction so that the ratio of H_2:CO did not fall below 5 (see, for example, DOS 2,212,700). If a lower ratio of H_2:CO is selected, the reaction is in general carried out with the addition of steam, in such large amounts that deposition of carbon on the catalyst, and hence a deactivation of the latter, are firmly prevented. Thus, for example, a value of 1:5.5 for the ratio of CO:H_2O has been mentioned (see, for example, DOS 2,345,230).

The setting of a certain CO:CO_2 ratio has also been regarded as necessary because a deactivation of the nickel on the catalyst occurs if the gas stream which is fed into, for example, a "wet" methanisation (i.e. methanisation with the addition of steam) contains only carbon dioxide. Against this, in the absence of carbon dioxide, there is a risk of depositing carbon on the catalyst, and this also deactivates the latter. It has therefore been proposed to maintain a ratio of between about 1:3 to about 3:1, preferably about 1:1, between the CO content and the CO_2 content of the gas. Methanisation in the presence of a customary catalyst containing less than 35% of nickel for a prolonged period has succeeded only when this ratio has been set (see, for example, DOS 2,345,230).

In addition to the wet methanisation, a "dry" methanisation (i.e. methanisation without the addition of steam), has also been described, but again only under certain conditions. Thus, this method of working is used only in order to increase the methane content of so-called rich gas, that is to say a gas which contains about 40—70% of methane and which has been obtained, for example, by an appropriately operated reforming of hydrocarbons or by wet methanisation, to, for example, 90% and above (see, for example, DOS 2,303,895). Furthermore, dry methanisation is in general carried out in the low temperature range of about 200—300° C, preferably in the presence of a catalyst with a high nickel content or of specially manufactured catalysts (see, for example, DOS 2,231,316).

Catalysts containing nickel have frequently been described for the reaction of low-boiling hydrocarbons in the presence of steam (steam reforming) to give gases containing methane. Thus, for example, catalysts with 25—65% of nickel on a silicate support with a predetermined internal surface (see DOS 1,545,428) and catalysts with 10—25% of nickel on aluminium oxide, which catalysts were obtained by precipitation of the catalyst substances, calcination at temperatures up to 495° C and subsequent reduction with hydrogen, (see DOS 1,770,426), have been described. Another catalyst, proposed for steam reforming and calcined at 900° C, consists of 3—80, preferably 12—31%, of nickel with additions of at least 0.5%, preferably 1—7%, of a potassium compound on a heat-resistant oxide material (see DAS 1,199,427). All these catalysts can also be employed for methanisation, but if so the pre-conditions mentioned above with respect to the CO content or the CO_2 content and the ratio of $CO:H_2O$ in the feed gas must be observed.

The present invention provides a modified process of the type described, which is carried out at elevated temperatures, generally from 200° C, to 900° C, in such a way that the restrictive conditions which have been explained can be entirely, or at least to a large extent, disregarded. According to the present invention there is provided a process for the manufacture of methane which comprises reacting, at an elevated temperature, hydrogen and an oxide of carbon in the presence of a catalyst which consists of an inert support, which is based on a metal oxide and is free from acid functions and which contains up to 30% by weight of nickel oxide, and which has been calcined at a temperature of at least 1,000° C.

Appropriately, the support of the catalyst employed in the process of this invention is calcined before applying a nickel salt, temperatures of at least 1,300° C, being preferred in order to ensure that the support is inert. Support materials which can be used are, in particular, aluminium oxides, such as sintered alumina, and also other refractory oxides or oxide mixtures, capable of being highly calcined, for example those of magnesium, calcium and silicon, optionally if desired with the addition of binders having as neutral a reaction as possible, such as calcium aluminate cement. The nickel oxide content of the catalyst is generally from 3 to 30% by weight, in particular 5 to 15% by weight. The application of the nickel to the support can be carried out in the customary manner, suitably by impregnation with a nickel salt solution, for example nickel nitrate solution, and subsequent decomposition of the salt; the catalyst can also be shaped in the customary manner. If necessary, the catalyst can be alkalised in the customary manner, preferably by means of potassium compounds which produce potassium oxide on calcination.

The methanisation can be carried out in known manner, generally in the temperature range from 350° to 950° C, or above and, if appropriate, under pressures of up to about 100 bars, particularly when a "wet" methanisation is being carried out. It is not usually necessary to arrange for a circulation of part of the product gas since it is possible, with the catalyst employed according to this invention, to process feed gases with high CO contents.

Because of the nickel content of the catalyst, the feed gas must naturally have the purity required as regards catalyst poisons, as is customary. The feed gas will generally contain CO; the content of CO in the feed gas is generally from 3 to 50% by volume. It is thus not necessary to reduce the CO content beforehand by shift conversion, as has been usual in the past. The CO_2 content of the feed gas has no essential importance. Gases which are virtually free from CO_2 can be processed.

It is a particular advantage of the process according to this invention that the addition of steam to the feed gas can be kept very low, that is to say the large excess of steam customarily employed is not necessary. If hydrogen is present in the feed gas in an amount which is at least stoichiometric with respect to the carbon present, an addition of less than 0.1, in particular less than 0.07, volume of steam per volume of dry feed gas suffices, in general, to ensure that there is no deposition of carbon on the catalyst. If hydrogen is present in a less than stoichiometric amount, it is appropriate to add more steam. However, this addition can in all cases be no more than 0.3 volume/volume of dry feed gas, that it to say considerably lower than is customary. Compared with known processes, this enables one to utilise the catalyst volume substantially better, in particular since the conversions over the catalysts employed according to this invention are in general higher than those over the methanisation catalysts used otherwise.

According to a further embodiment of this invention, the methanisation is carried out without the addition of steam, that is to say dry; thus, it is not necessary for the feed gases to contain about 40% by volume or more of methane, such as is the case with rich gases. In this procedure, it is also possible to recycle part of the product gas into the methanisation reactor by circulation in known manner, but in general this is not necessary. With the catalysts used according to this invention, in dry methanisation the reaction equilibria are set up, in a surprising manner and to an extent which largely corresponds to that theoretically expected, over the entire temperature range of 200° to 900° C, the process in general being carried out in the temperature range from 250° to 700° C. It is particularly surprising that, even in dry methanisation, the formation of carbon and a fall in the activity of the catalyst do not occur.

In this way, it becomes possible to eliminate any adverse influence of the added steam on the formation of methane and on the final concentration of methane and, at the same time, to obtain a reaction gas with a high final temperature.

The possibility of being able to carry out the methanisation without the addition of steam, using the customary temperature ranges and with virtually any feed gas composition, provides a substantial reduction in technical costs and hence a higher profitability for the process for the formation of methane from oxides of carbon and hydrogen.

The following Examples further illustrate the present invention.

EXAMPLE 1.

Gas mixtures, such as are obtained by the gasification of brown coal (lignite) or heavy oils after appropriate processing and purification, were methanised under a pressure of 30 bars over a catalyst which contained 14% of nickel on aluminium oxide and which had been calcined at a temperature from 1,300° to 1,350° C. In each case, the gas was passed into the reactor at an initial temperature of 350° C.

	Inlet gas				Outlet gas			
	I	II	III	IV	I	II	III	IV
Final reaction temperature °C (% by volume)					620	550	600	425
H_2	72.8	61.7	50.0	72.1	36.2	22.8	16.1	11.9
CO	21.0	15.2	50.0	22.0	2.0	1.1	5.2	0.3
CO_2	4.1	17.9	0	3.3	10.1	32.2	42.1	8.5
CH_4	2.1	2.2	0	2.6	51.7	43.9	36.6	79.3
steam addition volume/volumes of gas	0.1	0.3	0.3	0.1				

After 2,000 hours of operation, there was no fall in the activity of the catalyst in any of the cases.

EXAMPLE 2.

Various gas mixtures were reacted under a pressure of 30 bars over a catalyst based on an alumina/silica mixture with 12.5% of nickel, which catalyst had been calcined at a temperature from 1,275° to 1,300° C, without the addition of steam. The results thus obtained are summarised in the Table which follows:

Gas temperature °C		Inlet gas in % by volume				Outlet gas in % by volume			
Inlet	Outlet	CH_4	CO	CO_2	H_2	CH_4	CO	CO_2	H_2
490	600	–	24.8	–	75.2	60.4	0.8	7.2	31.6
400	550	–	24.6	–	75.4	67.7	0.7	5.6	26.0
250	300	–	25.1	–	74.9	95.1	0.2	0.8	3.9
480	620	4.0	19.1	3.9	73.0	60.0	1.5	6.9	31.6
450	630	41.6	5.2	7.6	45.6	56.4	1.7	7.3	34.6
450	725	26.4	10.2	5.8	57.6	40.6	5.3	7.7	46.4
240	300	83.0	0.1	3.2	13.7	96.1	0	0.8	3.1

Each of the experiments lasted 800 hours, without a fall in the activity of the catalyst being observed.

WHAT WE CLAIM IS:—

1. Process for the manufacture of methane which comprises reacting, at an elevated temperature hydrogen and an oxide of carbon in the presence of a catalyst which comprises an inert support which is a metal oxide free from

acid functions and which contains up to 30% by weight of nickel oxide, said support having been calcined at a temperature of at least 1,000° C.

2. Process according to claim 1, in which the inert support is aluminium oxide.

3. Process according to claim 1 or 2, in which the calcination is carried out at a temperature of at least 1,300° C.

4. Process according to any one of claims 1 to 3 in which the catalyst contains 5 to 15% by weight of nickel oxide.

5. Process according to any one of the preceding claims in which the catalyst also contains potassium oxide.

6. Process according to any one of the preceding claims which is carried out in the presence of not more than 0.3 parts by volume of steam per part by volume of dry feed gas.

7. Process according to claim 6, which is carried out at a temperature from 350° to 950° C.

8. Process according to any one of claims 1 to 5, which is carried out without the addition of steam.

9. Process according to claim 8 which is carried out at a temperature of 250° to 700° C.

10. Process according to claim 1 substantially as hereinbefore described.

11. Process according to claim 1 substantially as described in either of the Examples or part thereof.

12. Methane whenever manufactured by a process as claimed in any one of the preceding claims.

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