(12) UK Patent Application (19) GB (11) 2 077 613 A

(21) Application No 8114368
(22) Date of filing
11 May 1981
(30) Priority data
(31) 2169/80
(32) 19 May 1980
(33) Denmark (DK)
(43) Application published
23 Dec 1981
(51) INT CL^3 B01J 33/00
(52) Domestic classification
B1F D1X1
B1E 1162 1180 1203 1208 1298 1315 1331 1342 1463 1497 1513 1613 1623 1627 1631 1701 1705 1712 1714 1719 1722 1724 FK
(56) Documents cited
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GB 962893
(58) Field of search
B1E
B1F

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(54) A method and catalyst for exothermal catalytic gas phase reactions

(57) An exothermal catalytic gas phase reaction is conducted in a cooled reactor containing a bed of porous catalyst particles each having an outermost zone that has catalytic activity with respect to that reaction that is less than the catalytic activity of the remainder of the particle. Optionally, the pores in the outermost zone may contain a material catalytically active in a side-reaction. When the method is applied to methanation accompanied by a water gas reaction it is preferred to use, as the catalyst particles, particles comprising a porous support containing nickel and having copper in the outermost layer of each particle. Such catalysts are novel.

SPECIFICATION

A method and catalyst for exothermal catalytic gas phase reactions

The present invention relates to a method for carrying out exothermal catalytic gas phase reactions using a cooled reactor containing a fixed or fluid bed of a porous particulate catalyst which is active with respect to the desired reaction.

A large number of catalytic processes in the gaseous phase give a high heat generation, and in many cases they cause considerable rise in temperature. Examples thereof are the catalytic conversion of alcohols into hydrocarbons by the socalled Mobil synthesis, of carbon oxides by methanation into methane or by the Fischer-Tropsch synthesis into petrol and/or olefins (processes accompanied by the socalled water gas reaction); furthermore ammonia synthesis, preparation of formaldehyde from methanol, natural gas or othe hydrocarbons, and preparation of sulfuric acid vapour and sulfur trioxide from sulfur dioxide.

The high temperatures may involve a number of disadvantages. In many cases they can cause damage or destruction of the catalyst, e.g. by sintering of the active catalyst material or the pore system of the catalyst. Undesired side reactions may often take place, thus decomposition to free carbon by the preparation of hydrocarbons from carbon oxides or alcohols, which carbon may block and destroy the catalyst. In many cases the higher temperatures may shift the reaction equilibrium and selectivity in an undesired diection; thus in the Fischer-Tropsch synthesis high temperature favours the formation of methane at the expense of the desired products, e.g. ethane, ethene or other olefins or petrol.

Exothermal catalytic processes are often carried out in adiabatic reactors and in such cases one often attempts to limit the increase in temperature by diluting the reactnts, either with gases that are inert under the reaction conditions or by recycling product gas. Dilution with inert gases involves costs of the gases and of separating them from the end product, and recycling of product gas involves loss of energy in the recycling compressors.

In other cases exothermal processes therefore have been carried out in cooled reactors whereby dilution and the use of recycling compressors can be avoided. As cooling medium is used, i.a., air, salt baths, synthetic heat transfer media such as "Dowterm"® and in the above-mentioned hydrocarbon formation processes frequetly boiling water. In cooled reactors it is possible to obtain a low exit temperature of the product gases and thus an advantageous reaction equilibrium in cases where the desired product is favoured by low temperature. However, in cooled rectors with a catalyst bed it is not possible to avoid that shortly after the "ignition" of the reaction, i.e. a short distance from the inlet to the catalyst bed, a warm zone occurs, a socalled "hot spot" in which the temprature often will be near the temperature therodynamically determined by the adiabatic temperature increase. Only after this the reaction gas is cooled, i.e. further on in the catalyst bed. Accordingly, the same problems will occur as mentioned above with respect to the catalyst stability, possibly selectivity and carbon formation in case of hydrocarbon reactions.

The problems regarding the hot spot temperature have been treated in the literature, i.e., by van Welsenaere and Froment (Chemical Engineering Schience, Vol. 25, pp. 1503–1516, 1970) and it appears that hot spot is inevitable in tube reactors with constant wall temperature and that the hot spot temperatue is very sensitive to small variations in the process variables such as inlet temperature, concentration of the reactants and wall temperature. Accordingly there is a risk that the temperature may increase in an uncontrollable manner leading to socalled "runaway". Welsenaere and Froment state how the reactions can be controlled under given conditions, for example when carried out in a fixed catalyst bed arranged in tubes surrounded by a cooling medium; a critical factor in this case is the tube diameter. In said paper Welsenaere and Froment give results for the oxidation of p-xylene to phtalic acid anhydride at atmospheric pressure and with a large excess of air.

The calculations have been made for an irreversible process of first order, but can also be transferred without substantial alterations to reversible reactions which are not of first order. Hereby one finds e.g. for the methanation reactions

(1) $CO + 3H_2 \rightleftarrows CH_4 + H_2O + 49$ Kcal/mol,
(2) $2CO + 2H_2 \rightleftarrows CH_4 + CO_2 + 59$ Kcal/mol, and
(3) $CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O + 39$ Kcal/mol,

that the diameter of the catalyst tubes cannot be more than a few millimeters if there shall be complete security against runaway under any conditions. Such small tube diameter is inapplicable to industrial operation. The most important difference between the example of Welsenaere and Froment and the methanation reactions seems to be the high pressure and the high molar concentration in the latter and the resulting high production of heat per catalyst volume unit. Similar conditions apply to other hydrocarbon-forming reactions, e.g. the Fischer-Tropsch synthesis for the formation of petrol and/or olefins:

(4) $nCO + 2nH_2 \rightleftarrows (CH_2)_n + H_2O$ + ablut 40 Kcal/gram atom C

or the socalled Mobil synthesis for the formation of hydrocarbons from alcohols, e.g.

(5) $nCH_3OH \rightarrow (CH_2)_n + nH_2O$ + about 12 Kcal/gram atom C

Thus, it is not possible without special measures to prevent an increase of temperature to that or a value near that determined by the adiabatic temperature increase for such reactions. Weisenaere and Froment suggest a dilution of the catalyst filling in the catalyst bed, e.g. with catalytically inert filler bodies whereby the amount of heat produced per rector unit volume decreases. However, it is found that a relatively high degree of dilution of the catalyst is necessary, which necessitates an increase of the catalyst volume itself in order to "ignite" the reaction. Thus, this method has the drawback of demanding an enlargement of the reactor and thus an increase of the capital costs; more important is often the fact that the dilution has the disadvantage of decreasing the resistance of the catalyst filling or its adsorption capacity for catalyst poisons carried on with the reaction flow. Therefore, such dilution of the catalyst is not a satisfactory solution of the temperature control problems in the cooled exothermal catalytic processes.

In order to study the problems further some experiments were carried out in an air-cooled methanation reactor with a catalyst having the manufacturing designation MCR–2X. This is a microporous, temperature-stable, mechanically strong catalyst with nickel crystallites of the same order of magnitude as the pore diameter, on a support of γ-alumina (see Karsten Pedersen, Allan Skov and J.R. Rostrup-Nielsen, ACS Symposium, Houston, March 1980). The catalyst was used in the form of cylinders with height and diameter 4.3 mm. In some of the experiments the catalyst was diluted with catalytically inactive cylinders of same geometric shape. The pressure in the reactor was maintained at 26 kg/cm^2 and a feed gas was used of the composition 70% H_2, 9% CO, 10% CO_2 and 11% CH_4. These experimental conditions will give thermodynamically determined adiabatic increases of temperature of between 380 and 400°C irrespective of the degree of dilution of the catalyst.

It was found that without dilution of the catalyst it was not possible to limit the temperature increase which accordingly became the said 380 to 400°C. With dilution ratios of 1:3 and 1:5 (i.e. a volume of inert cylinders 3 and 5 times, respectively, that of catalyst bodies) actual increases of temperature were until 50°C less than the expected adiabatic temperature increases of 380 to 400°C. In these experiments the temperature of the tube wall in the hot spot area was about 600°C or more, which would be an unrealistic high tube wall temperature in industrial operation; in an industrial cooled reactor the highest tube wall temperature would not exceed 400°C. The limitation of temperature increase obtained can be considered substantial although in itself it has no big practical industrial importance, and although catalyst dilution in this manner for the above reasons is not very expedient.

However, a detailed analysis of the reduced temperature increase demonstrated that the reduced temperature increase resulted from the fact that the reaction velocity had not increased as much as was to be expected according to the reaction kinetics, and surprisingly it was found that this reduced reaction velocity was due to the fact that the calculated reaction velocity at high temperature exceeds the velocity of diffusion of the reactants through the gas film surrounding the catalyst particles. Since the gas phase diffusion is almost independent of the temperature (activation energy 1–2 Kcal/mol), the reaction velocity ran against a barrier caused by the lacking presence of reactants at the actual reaction sites, the interior of the catalyst bodies, and therefore the reaction is prevented from runaway.

It is the object of the invention to utilize this surprising observation to indicate how one can generally prevent runaway in catalyzed exothermal gas phase reactions in cooled reactors containing a bed of porous particulate catalyst which is active with respect to the desired reaction. In accordance with the invention this is achieved when each of the individual particles of the catalyst outermost has a zone of reduced catalytic activity with respect to the desired reaction.

The outermost part of each individual catalyst particle thus can consist of a completely inert layer or of a layer with reduced activity for the strongly exothermal reaction in question. In case of simultaneously occurrence of a strongly exothermal main reaction together with one or more side reactions (which may be less exothermal, or even thermally neutral or endothermal), the outer layer may, if desired, be catalytically active for the side reaction but not for the main reaction; as an example can be mentioned that the above reactions (1), (2) and (4), which are catalyzed by nickel, are accompanied by the water gas reaction, also called the shift reaction:

(6) $CO + H_2O \rightleftarrows CO_2 + H_2$ + 10 Kcal/mol,

which, i.a., is catalyzed by copper.

Whether the outer layer is catalytically inert or catalytically active with respect to a side reaction but inactive with respect to the main reaction, the abovementioned film diffusion is extended to also include diffusion through the inert outer layer of the catalyst. Therefore, it will be possible to determine the maximum reaction rate in the reactor since it is determined by the thickness of the inert layer. The thickness of the layer inert to the main reaction in practice will be from one to a few orders of magnitude bigger than the thickness of the surrounding gas film; on basis of calculations the thickness of this gas film can be estimated at about 1 μ at normal industrial conditions; according to the invention said outer zone of the catalyst particles therefore can suitably have a thickness of 0.01–2 mm. Thicknesses of said layer of more than about 0.5 or 1 mm will in practice only come into question when using comparatively large catalyst particles.

A general explanation of the invention as defined is that a given catalyst body with homogeneous activity and a homogeneous pore system exposed to a given mixture of reactants is subjected to various reaction restrictions as the reaction temperature is changed (increased).

At low temperature the reaction rate is limited by the catalyst material. Here, the reaction is in the socalled intrinsic velocity rnge in which there is almost no concentration gradient of the reactants through the pore system of the catalyst body. As the temperature increases the catalyst activity increases, and this imparts an increased gradient of the reactants thrugh the catalyst bodies. At some point a temperature range is reached where the diffusion of the reactants thrugh the catalyst bodies becomes the limiting parameter for the reaction rate; in effect this means that not all of the catalyst material is used in the reaction; the efficiency factor becomes <1.

When the temperature is further increased, the parameter determining the reaction rate will be the mass transport through the gas film surrounding the catalyst bodies. Normally this rate is too large for the cooling surface of the reactor to limit the hot spot temperature to a level substantially below that determined by the adiabatic temperature increase, which in many cases means that a thermal sintering cannot be avoided or in case of cetain methanation reactions that carbon formation cannot be prevented.

According to the invention, however, a restrictive surface is incorporated into the individual catalyst bodies by increasing the gas film or by decreasing in some way the penetrative power of the reactants whereby the reaction rate and accordingly also the temperature increase is limited.

It could be expected that the incorporation of such inert layer, "delaying layer", would cause difficulties in the start or "ignition" of the exothermal reactions. However, this does not happen because the reaction rate is slow in the ingnition zone under any circumstances so that the gas diffusion through the inert layer will not be restrictive (determining) for the reaction rate. This layer will only become a limiting factor, i.e. virtually it will only begin to be effective when the reaction rate becomes so high that it is desired to slow it down. As the inert layer constitutes only a small part of the catalyst pellet the resistance of the catalyst against poisoning is retained.

In this connection it can be mentioned that said outer layer on very small catalyst pellets may constitute above 50% of their volume; but normally its share will be considerably less, for instance for cylindrical catalyst bodies with height and diameter of 4.2 mm typically 1–10%, especially 2–10% and frequently 2–5% of the volume.

The reactor may be any type of cooled reactor for exothermal reactions, for example a tubular reactor or a reactor having a larger space of optional shape and containing cooling tubes wherein a cooling medium flows. The catalyst bed usually will be a socalled fixed bed but the invention can also be used in connection with catalysts in fluid bed.

As mentioned the outer layer must have reduced catalytic activity and although it will often in accordance with the invention be suitable to use a catalyst the individual particles of which outermost have a zone which is inactive with respect to the desired reaction (or main reaction), it may in some cases be expedient to use a catalyst wherein said outer zone has some yet reduced activity with respect to the reaction (or main reaction).

The outer zone can be provided in various ways, frequently in analogy with technique known from the pharmaceutical industry where tablets are prepared with more layers of varying composition or varying concentrations of an active substance.

Thus, it is possible to first prepare catalyst bodies of the normal kind, consisting of a porous support containing catalytically active material in the pore system. This can be prepared by known technique, for example by coprecipitation or by first preparing porous support bodies which are then impregnated with the catalytically active material. The catalyst thus prepared is then immersed in a gel or sol of inert support material of the same or another kind as that of the catalyst support itself. If the outer layer should not be completely catalytically inert but should have restricted catalytical activity, it can then be impregnated while ensuring that the concentration of catalytically active material becomes lower than that in the inner layer.

Alternating impregnations, washing out and treatments with chemicals can be combined whereby a desired structure and combination of structures can be obtained. On a finished catalyst an inert layer or even a catalytically active layer partially clogging the pore orifices can be applied, e.g. by electrolysis or depositing from the vapour phase, whereby catalyst activity in the outer layer and the diffusion rate into the interior of the catalyst are reduced. A special structure can be obtained by pelletizing a mixture of disintegrated catalyst particles with an inert support material. Hereby the diffusion effect is combined with a dilution of the catalyst, whereby the degree of dilution can be reduced substantially.

Practical embodiments of these methods and combinations thereof will be obvious to those skilled in the art.

As mentioned the principle disclosed may be utilized not only in case of a single exothermal reaction but also in cases where an exothermal main reaction and one or more side ractions occur simultaneously in the same reactor which contains a bed of a particulate catalyst which is active with respect to the main reaction. In that case each of the individual particles of said catalyst according to the invention outermost has a zone of a material which is at leas partially inactive with respect to the main reaction but catalytically active with respect to one or more side reactions.

A practical embodiment of such a catalyst, or generally of catalysts in accordance with the principles of the invention, is a catalyst whose particles consist of a porous support material which is catalytically inactive with respect to the desired reaction or main reaction (but possibly catalytically active with respect to a side reaction) and contain in part of the pore system a material which is catalytically active with respect to the desired reaction or main reaction, in such a manner that the pores in the outer zone of the support particles are free of the material which is catalytically active with respect to the desired reaction or main reaction. The content in the pores of catalytically active material may for example be provided by co-precipitation, by electrolysis, by depositing from the vapour phase or by impregnation from the liquid phase.

In cases where the catalyst is only to be catalytically active with respect to one reaction, the catalyst particles may according to the invention consist of a porous, inactive material which contains in part of the pore system a material which is catalytically active with respect to the desired reaction, the pores in the outer zone of the support being partially blocked by catalytically inactive material.

In another embodiment of the method, which is applicable both in cases where only one reaction is catalyzed and in cases where a main reaction as well as one or more side reactions are catalyzed by different components of the catalyst, the catalyst employed has the structure of "islets" embedded in the main structure of the porous support. In that case the catalyst particles in accordance with the invention consist of a porous support material which may in itself be catalytically active or may comprise a component which is catalytically active with respect to one or more desired side reactions, the particles having such a structure that "islets" of the support having a high content in the pores of a material which is active with respect to the desired reaction or main reaction are statistically evenly distributed in the interior of the catayst, by more sparingly present or absent in the outer zone of the catalyst.

Catalysts prepared according to the described principles can be used with particular advantage for hydrocarbon reactions such as those shown hereinbefore, especially methanation reactions. The catalyst may then consist of a known support material, e.g. γ-alumina, magnesium aluminium spinel, silica, zirconia, titania or combinations of two or more of these materials, together with catalytically active nickel, whereby there outermost is a zone without nickel or with a reduced concentration of nickel. In this way the desired shell effect is obtained directly.

However, the principle may be used even more elegantly; as mentioned above reactions (1), (2) and (4) are accompanied by the water gas reaction (6). The reactions (1)–(4) and also the water gas reaction are catalyzed by nickel whereas the water gas reaction is also catalyzed, i.a., by copper. It is advantageous to have the methanation reactions accompanied by the water gas or shift reaction in such a manner that the partial pressure of carbon monoxide is reduced before it comes too much into contact with the catalyst nickel since CO to some extent is a catalyst poison for nickel and the poisoning can be reduced by reducing the partial pressure of CO. It should be noted that it is nickel metal and copper metal that catalyze the reactions whereas the catalyst metal is applied in the form of a compound, commonly a nitrate or hydroxide, which is later oxygenated, e.g. by calcination, and finally reduced to the free metal, frequently during the start of the desired reaction by the aid of hydrogen present amongst the reactants; these circumstances will be ignored hereinafter and the specification will only deal with the free metals.

It is known that alloys of copper and nickel above a certain copper content show a very poor activity for methanation (see M. Araki and V. Ponec, J. Catalysis 44, 439 (1976)); this is further illustrated in Example 1 hereinafter. However, the Ni/Cu-catalyst still has activity for the conersion of carbon monoxide into carbon dioxide by the water gas reaction (6). This can be utilized in connection with the present invention by the preparation of a nickel catalyst outermost having a shell of the nickel-copper alloy. In this way there is firstly obtained a slowing down of the strongly heat-evolving methanation reaction but also a reduction of the partial pressure of the carbon monoxide by the water gas reaction, whereby the nickel-containing catalyst core is spared the socalled β-desactivation (see the abovementioned paper by Karsten Pedersen, Allan Skov and J.R. Rostrup-Nielson in ACS-symposium). By the β-desactivation the adsorbed carbon monoxide is slowly converted into deposits of carbon having low reactivity, which desactivates the catalyst, but this is avoided when using according to the invention nickel-containing porous catalyst particles containing copper in the outer layer of each particle.

The outer copper-containing catalyst film can be formed by various means. For example one can first prepare particles of a nickel catalyst in known manner, e.g. by impregnation or co-precipitation, and then immerse the particles in water or other liquid and subsequently in an impregnation liquid containing a copper compound, e.g. copper nitrate or hydroxide.

Another method consists in precipitating copper hydroxide from copper nitrate in the outer parts of the pore system of the catalyst. In this method it is advantageous if the support material is basic, for example contains free magnesium oxide. This can for instance be obtained by using a support of magnesium aluminium spinel which is burned at such temperature (about 1100°C) that unreacted magnesium oxide still possesses some reactivity. Alternatively, the pore system is first filled with suspended magnesium oxide or other base such as calcium oxide or solutions of an alkali metal hydroxide. Copper hydroxide will be precipitated in the outer part of the pore system according to the reaction

(7) $Cu(NO_3)_2 + MgO + H_2O \rightarrow Cu(OH)_2 + Mg(NO_3)_2$

The method described can be used with nickel catalysts wherein the nickel has been evenly distributed by other means, as mentioned for example by co-precipitation, impregnation with nickel nitrate without the presence of MgO or other alkaline compounds in the pore system. If the catalyst support contains free magnesium ocide or other alkaline compounds, nickel can be applied before or after copper by impregnation with nickel hexamine formate, which in itself is alkaline but does not cause precipitation of nickel by contact with alkaline compounds. In this way it is possible to control the ratio nickel to copper in the outer zone of the catalyst and at the same time obtain an even distribution of the nickel content.

The reaction velocity in methanation and thereby the reaction temperature can be controlled according to similar principles using a vanadium- or molybdenum-based catalyst in a sulfur-containing atmosphere as described in British patent application No. 80,40165.

It may be particularly useful to utilize the principle of the present invention in connection with the process described in British patent application No. 80,40166 for preparing a gas mixture having a high content of C_2-hydrocarbons by reacting a feed gas mixture containing hydrogen and carbon oxides by means of a catalyst containing molybdenum and/or vanadium and iron and/or nickel in the presence of gaseous sulfur compounds. This reaction is a Fischer-Tropsch synthesis and it is very important to maintain the temperature relatively low because higher temperatures will shift the equilibrium towards the production of methane. Therefore, in accordance with the present invention the catalyst bodies may be provided with a shell of inactive support material or a shell containing copper to synthesize the simultaneous water gas reaction.

The method of the invention will be illustrated in the following by some Examples.

Example 1

A. A series of catalysts were prepared by co-precipating sodium silicate and varying amounts of copper and nickel nitrates with sodium hydrogen carbonate.

The precipitated product was shaped to particles which were washed out to remove sodium compounds, dried at 120°C, calcined at 500°C and reduced in hydrogen at 500°C. The methanation activity was measured at 1 atm and 250°C by passing a gas consisting of 1% CO in H_2 in an amount of 100 Nl/h over the catalyst in form of irregular bodies having the size (determined by sieve) of 0.3–0.5 mm. The following results were obtained:

Catalyst No.	Weight % Ni	Cu	Atomic ratio Ni/Cu + Ni	Activity 10^{-3} mol/g/h
1	68.5	0	1.0	93.75
2	54.2	14.6	0.8	22.32
3	40.2	29.0	0.6	8.93
4	26.5	43.0	0.4	3.57
5	13.1	58.7	0.2	0.89
6	0	70.1	0	0

It appears that even a small amount of copper drastically reduces the methanation activity.

B. 3 Catalysts were prepared by impregnating a support of γ-alumina having an internal surface area of about 40 m^2/g in solutions of copper nitrate, nickel nitrate and a mixture of nickel nitrate and copper nitrate, respectively. The impregnated supports were calcinated at 550°C and reduced in hydrogen at 720°C. The catalysts were tested in a reactor at a pressure of 1 atm with 53.5 Nl/h gas consisting of 61.8% by volume of H_2, 18.2% by volume of H_2O and 20.0% by volume of CO, over 0.2 g catalyst as particles of 0.3–0.5 mm. In this way the following rates for carbon monoxide conversion (water gas reaction, shift reaction) and methanation, were measured:

	reaction rate at 375°C 10^{-3} mol/g/h shift	methanation
Cu	1.05	0
Ni, Cu	73	5.2
Ni+)	—	43
Ni++)	1431	1608

+) measured at 311°C as reactor temperature could not be controlled at 375°C
++) measured on the above mentioned catalyst MCR-2X.

It appears that the Ni, Cu-catalyst has a good activity for the water gas reaction whereas none of the Cu-containing catalysts have any significant activity for methanation.

Example 2

A support consisting of magnesia with a minor content of alumina (ratio Mg/Al 7:1) in the form of cylinders with height and diameter 4.5 mm was impregnated with a saturatet aqueous solution of copper nitrate. The impregnated support was calcined at 550°C. When the particles were broken it could be clearly seen that copper had accumulated as a thin black shell on the outside of the support. Microscopic examination showed that the thickness of the layer was about 50 μ.

The copper-impregnated support was impregnated with a saturated aqueous solution of nickel hexamine formate prepared by dissolving 23 g nickel formate in 50 ml concentrated aqueous ammonia. The impregnated catalyst was calcined at 300°C. The broken particles showed even colouring and thus even distribution of nickel. By analysis 0.6% by weight of Cu and 2.7% by weight of Ni were found.

A corresponding catalyst was prepared by impregnating first in nickel hexamine formate and then copper nitrate. The copper shell appeared as a dark colouring of the outer zone of the particles. This catalyst is designated catalyst A and as reference a copper free methanation catalyst, designated catalyst B, was prepared by impregnating the support in nickel hexamine formate.

Example 3

A methanation catalyst containing about 25% by weight of nickel on a stabilized support of alumina was impregnated in the form of 4.2 × 4.2 mm cylinders in a gel of alumina prepared by suspending 11 g alumina in 180 ml water and gelled with 5.6 ml concentrated nitric acid. The impregnated catalyst was calcined at 550°C.

A corresponding preparation was carried out with the difference that 10 ml of the alumina gel was mixed at beforehand with a solution of copper nitrate. The impregnated and calcined catalyst showed an outer shell containing copper, by microscopic examination estimated at a thickness of about 0.5 mm. Minor amounts of copper nitrate had penetrated into the interior of the catalyst but the ratio between the copper content in the outer zone and that of the interior could be estimated at about 3:1. This catalyst is designated C.

Example 4

This experiment shows how a coating on a catalyst applied by means of a gel can reduce the reaction rate at high temperature.

A methanation catalyst with nickel in form of 4.2 × 4.2 mm cylinders was coated with a gel of alumina and then dried. Then the catalyst was reduced in pure hydrogen at 800°C for 2 hours. This catalyst is designated D.

A catalyst without such coating was activated (reduced) in the same manner. It is designated E and is identical with the abovementioned catalyst MCR-2X.

Example 5

The present example illustrates the testing of catalyst A-E mentioned in Examples 2 to 4.

The catalyst pellet to be tested was fixed between two thermoelements in a tube reactor having an internal diameter of 6 mm. Then it was heated in pure hydrogen to about 300°C in order to eliminate possible traces of nickel oxide. Thereafter the hydrogen supply was cut off and the system fed with a synthesis gas consisting of 9% CO in H_2 at a rate of about 100 Nl/h during the entire experiment. At about 300°C the product gas stream was analyzed on a gas chromatograph and the amount of methane produced determined. Then the temperature was increased stepwise and the methanation rate determined at each step.

The table below demonstrates that catalysts having an inert outer layer applied with the gel have a reduced reaction rate at high temperature as compared with the homogenous reference catalyst.

Table 3

Catalyst	Test temp. °C	Methanation activity millimol/g/h
A Al_2O_3.MgO support impregnated with copper nitrate and nickel hexamine formate	300	1.4
	360	4
	417	6
	518	12
	603	11
	678	12
B Al_2O_3.MgO support impregnated with nickel hexamine formate	346	18
	389	60
	482	180
	577	250
	715	240
C NiO.Al_2O_3 catalyst coated with Al_2O_3	330	55
	425	95
	570	130
	741	95
D NiO.Al_2O_3 catalyst coated with a shell containing copper oxide and Al_2O_3	243	3.5
	295	30
	336	50
	440	65
	597	60
E NiO.Al_2O_3 catalyst (the above mentioned known catalyst MCR-2X without restrictions)	274	80
	323	180
	379	250
	438	270
	508	315
	569	310

The reason why catalysts B and E have maximum activities in the temperature range considered is the thickness of the gas film during the test, wherein the gas velocities have been considerably lower than by industrial operation; in normal industrial operation with the higher gas velocities, the gas film would become thinner and thereby slow the diffusion down to a lesser degree. The mass transfer value for the gas film is estimated at about 7 kmol/h/m², whereas this value would be about 100 kmol/h/m² under industrial conditions. This involves that the difference in high-temperature activity with and without shell will be higher than shown in table 3.

CLAIMS

1. A method in which an exothermal catalytic gasphase reaction is conducted in a cooled reactor containing a bed of porous catalyst particles that are active with respect to the desired reaction and that comprise particles that each have an outermost zone that has a catalytic activity with respect to the desired reaction that is less than the catalytic activity of the

remainder of the particles.

2. A method according to claim 1 in which the outermost zone is catalytically inactive with respect to the said desired reaction.

3. A method according to claim 1 or claim 2 in which the said outer zone has a thickness of 0.01 to 2 mm.

4. A method according to any preceding claim in which the said outer zone occupies from 1 to 10% by volume of the particle.

5. A method according to any preceding claim comprising the preliminary step of charging into the reactor the porous catalytic particles that have the said outermost zone of less activity.

6. A method according to any preceding claim in which the said particles each comprise a porous support that is inactive to the said desired reaction and in which pores of the support include a material that is catalytically active to the said desired reaction but the pores in the outermost zone are substantially free of the said material.

7. A method according to any of claims 1 to 5 in which the said particles comprise a porous support that is inactive to the said desired reaction and in which pores of the support include a material that is catalytically active to the desired reaction and the pores in the outermost zone are partially blocked by catalytically inactive material.

8. A method according to any preceding claim in which a side reaction is carried out in the reactor substantially simultaneously with the desired reaction and in which the said outermost zone includes a material that is catalytically active with respect to the side reaction.

9. A method according to any preceding claim in which the said particles include a material that is catalytically active with respect to the desired reaction and which is present in statistically evenly distributed islets within the interior of the particles, the outermost zone of the particles being free of this material or containing less of this material.

10. A method according to any preceding claim for carrying out a methanation reaction accompanied by a water gas reaction in which the bed comprises porous catalyst particles that each contain nickel in the pores of the support and have an outermost zone containing copper.

11. A method according to any preceding claim in which substantially all the catalytically active particles in the bed are particles that are active with respect to the desired reaction and that have the said outermost zone.

12. A method according to any preceding claim in which substantially all the particles in the bed are particles that are active with respect to the desired reaction and that have the said outermost zone.

13. A catalyst suitable for use in a method according to claim 10 comprising a particulate porous support containing nickel and having an outer zone containing copper.

14. A method for preparing a catalyst according to claim 13 comprising forming a support material comprising an alkaline material and containing nickel or nickel oxide by impregnation or precipitation from the vapour phase or by coprecipitation of the support material and material providing the nickel or nickel oxide, and treating the support material with a solution of a copper salt and thereby precipitating copper hydroxide in the outermost zone, and then drying, calcining and reducing the catalyst.

15. A method according to claim 14 in which the support material comprises active MgO.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon) Ltd.—1981.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.