BESCHWERDEKAMMERN DES EUROPÄISCHEN PATENTAMTS

BOARDS OF APPEAL OF THE EUROPEAN PATENT OFFICE

CHAMBRES DE RECOURS DE L'OFFICE EUROPEEN DES BREVETS

Internal distribution code:
(A) [ ] Publication in OJ
(B) [ ] To Chairmen and Members
(C) [X] To Chairmen
(D) [ ] No distribution

DECISION
of 24 October 2001

Case Number: T 0086/00 - 3.3.5

Application Number: 94917197.9

Publication Number: 0738235

IPC: C01B 3/38

Language of the proceedings: EN

Title of invention:
Process for the production of hydrogen/carbon monoxide mixtures or hydrogen from methane

Patentee:
GASTEC N.V.

Opponent:
BASF Aktiengesellschaft

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step (yes)"

Decisions cited:
-

Catchword:
-

Europäisches Patentamt | **European Patent Office** | **Office européen des brevets**
Beschwerdekammern | Boards of Appeal | Chambres de recours

Case Number: T 0086/00 - 3.3.5

DECISION
of the Technical Board of Appeal 3.3.5
of 24 October 2001

Appellant: (Opponent)	BASF Aktiengesellschaft Carl-Bosch-Strasse 38 D-67056 Ludwigshafen (DE)
Representative:	Isenbruck, Günter, Dr. Patent- und Rechtsanwälte Bardehle, Pagenberg, Dost, Altenburg, Geissler, Isenbruck Theodor-Heuss-Anlage 12 D-68165 Mannheim (DE)
Respondent: (Proprietor of the patent)	GASTEC N.V. Wilmersdorf 50 NL-7327 AC Apeldoorn (NL)
Representative:	Smulders, Theodorus A.H.J., Ir. Vereenigde Postbus 87930 NL-2508 DH Den Haag (NL)

Decision under appeal: **Decision of the Opposition Division of the European Patent Office posted 11 November 1999 rejecting the opposition filed against European patent No. 0 738 235 pursuant to Article 102(2) EPC.**

Composition of the Board:

Chairman: R. K. Spangenberg
Members: M. M. Eberhard
M. B. Günzel

Summary of Facts and Submissions

I. European patent No. 738 235 based on application No. 94 917 197.9 was granted on the basis of 14 claims. Claim 1 reads as follows:

"1. A process for endothermic catalytic conversion of gaseous hydrocarbons with steam to form a gaseous mixture which contains hydrogen, utilizing a reform catalyst based on nickel which is provided on a thermostable support, wherein at least 90% of the nickel particles (based on the number) are smaller than 10 nm and at least a part of the thermal energy required for the endothermic conversion is generated in the reaction mixture through a controlled catalytic reaction of a part of the hydrocarbon with oxygen.

II. The appellant (opponent) filed a notice of opposition requesting revocation of the patent on the grounds of lack of novelty and lack of inventive step. The following documents were relied upon during the opposition proceedings:

D1: GB-A-2 247 465

D2: Ind. Eng. Chem. Res., 1988, vol. 27, 790-795

D3: EP-A-0 112 613 (cited by the opposition division)

D4: Journal of Catalysis, 54, 1978, 207-218

III. The opposition division decided to reject the opposition. It pointed out in its decision that according to the patent in suit and to D3, commercially available nickel steam reforming catalysts could not be used in the autothermal reforming processes of D3 or D1 because of carbon deposits on the catalyst. The claimed process had surprisingly overcome the carbon deposit problem by using a Ni based catalyst having at least 90% of the Ni particles smaller than 10 nm. It could be inferred from D4 that the "Van Dillen" catalyst used in D2 had the claimed particle-size distribution. The opposition division took the view that the skilled person would not have combined the teachings of D1 and D2 because D1 or D3 taught away from using a nickel reforming catalyst and D2 did not disclose that the nickel reforming catalysts were good catalysts as regards stability and activity or were better catalysts than the Pt reforming catalysts of D1.

IV. The appellant lodged an appeal against this decision and cited a new document D5 in the grounds of appeal, namely Applied Catalysis, 10 (1984) 273-239. Oral proceedings took place on 24 October 2001.

V. The appellant's arguments can be summarised as follows:

D1 as well as D2 could be considered as representing the closest prior art. D1 disclosed all the features of claim 1 except the particle-size distribution of the Ni particles. Starting from D1 as the closest prior art, it was obvious to the skilled person to use the catalyst of D2 in the autothermal reforming process of D1. The catalyst of D2 had a Ni particle-size distribution falling within the definition of claim 1. This could be inferred from D2 itself which disclosed a Ni crystallite-size of 1-2 nm and a narrow crystallite-size distribution and further stated that no carbon overlayer was formed. This was confirmed by the particle-size distribution shown in D4 for catalysts which were prepared by exactly the same type of preparation as in D2. Figure 4 of D4 showed that particle sizes of up to 14 nm could be determined by magnetic measurements. D2 taught that no deposition of carbon occurred with the catalyst disclosed therein and both D1 and D2 concerned steam reforming. Thus, D2 gave the skilled person all the characteristics necessary to reduce the carbon deposition in the steam reforming reaction. Starting from D2 as the closest prior art, the only missing feature with respect to the claimed process was that the energy required for the endothermic reaction was produced internally. As according to D2 no carbon deposition occurred with the catalyst described therein, it would have been obvious to the skilled person to use this catalyst in the two-step process of D1 to reduce carbon deposition. D2 disclosed that the catalyst showed an irreversible deactivation at a steam/methane ratio of 5.7; however such a high ratio was not usually applied. D2 taught that, at a lower ratio, the catalyst activity could not be regained once the reaction was stopped. However, this would not have deterred the skilled person from using the catalyst of D2 in a technical process since the process was normally not stopped and, thus, the risks were not high. Nickel catalysts being in general less expensive than catalysts containing a metal of the platinum group, the skilled person would have used the nickel catalysts of D2 in the process of D1. It was further known from D5 that the deposition of carbon on the reforming catalyst could be avoided at steam/carbon ratios of 1.5 to 3 with a Ni catalyst having a mean size of the nickel crystallites of less than 10 nm. On the contrary carbon deposition occurred with catalysts having a higher Ni particle mean size, and the carbon deposition was more important the greater the mean size. Therefore, D5 confirmed that it was obvious to the skilled person to use nickel catalysts having a nickel crystallite size < 10nm as the reforming catalyst in a steam reforming reaction, and thus, also in the process of D1, in order to avoid the deposition of carbon on the catalyst.

Furthermore there were serious doubts that the examples of the patent in suit supported claim 1 and the alleged inventiveness thereof. In all the examples no steam was added although according to column 6 of the patent in suit the methane should react with steam. With 2 volumes of CH_4 and 1 volume of oxygen as used in all the examples the oxidation process did not give steam. The examples also did not support or illustrate the claimed particle-size distribution and in particular the preferred particle size of smaller than 5 nm.

VI. The respondent (proprietor of the patent) presented inter alia the following arguments:

Regarding the question whether or not steam was produced in the examples of the patent in suit, it was clear that steam was generated in the oxidation step as taught for example in D1. Although a methane/oxygen ratio of 2:1 was used in the said examples, it was indicated in column 6 of the patent in suit that oxygen was also incorporated in the oxidation catalyst and that at high temperature reduction of the metal oxide by the methane occurred readily.

D5 was not more relevant than the documents already on file. It gave no indication about the particle-size distribution of the nickel crystallites. D5 disclosed conflicting data in Figures 2 and 3 as regards the relation between the mean Ni particle size and the coking rate. Furthermore it taught that the resistance to coking of the nickel catalyst was determined by the quantitative ratio of the nickel phase and the NiO+MgO mixture as well as the chemical composition of the NiO+MgO mixture. Therefore, D5 would have rather pointed the skilled person in another direction. D2 was not the closest prior art since it did not relate to internal heat generation. Starting from D1 or D3 as the closest prior art, the present invention dealt with the problem of formation of filamentary coal growing from the Ni particles, which caused disintegration of the catalyst. D1 and D3 showed that both precious metal and nickel catalysts were known and that a precious metal catalyst should be used for the steam reforming process. The teaching of D2 was rather conflicting. Furthermore, the appellant did not provide evidence that the catalyst prepared in accordance with D2 indeed met the criteria of the particle-size distribution. D4 showed a narrow particle-size distribution; however it was well-known that the magnetic measurements were unsuitable to determine small amounts of large particles. D2 taught that the catalyst as prepared by the authors of D2 tended to deactivate and seemed to be deactivated by the presence of a nickel hydrosilicate film on the particles when used at high steam/methane ratios. Furthermore in the case of a low steam/methane ratio D2 taught that the catalyst activity could not be regained once the reaction was stopped. Although one would normally not intend to stop the industrial process, the latter had, however, to be stopped for maintenance or for replacing a part of the catalyst or for other unscheduled reasons, and then the whole catalyst had to be changed which resulted in increased costs. Therefore, the skilled person looking for a solution to the problem of formation of filamentary carbon would not have considered using the Ni catalyst described in D2. D2 would not have led the skilled person to go away from the precious metal catalysts of D1/D3.

VII. The appellant requested that the decision under appeal be set aside and that the patent be revoked. The respondent requested that the appeal be dismissed.

Reasons for the Decision

1. The appeal is admissible.

2. The process according to claim 1 is new over the disclosure of the cited documents. This was not disputed by the appellant.

3. The question arises which of documents D1, D2 and D3 represents the closest prior art. D2, contrary to the claimed process, does not relate to an autothermal reforming process, ie a process in which at least a part of the thermal energy required for the steam reforming reaction is generated in the reaction system by the exothermic oxidation of a part of the hydrocarbon with oxygen. Furthermore, D2 does not deal with the problem of carbon deposition on the nickel catalyst, which is addressed in the patent in suit and in D3. It merely mentions that the permanent deactivation of the catalyst used at a high steam/methane ratio was due to the formation of a nickel hydrosilicate layer and not to a carbon overlayer (see abstract and page 794, right-hand column, 4th paragraph). In contrast thereto, D1 and D3

concern an autothermal reforming process, like claim 1. Furthermore, D3 discloses an example using a commercially available nickel steam reforming catalyst and addresses, like the patent in suit, the problem of carbon or soot accumulation on the nickel catalyst. Although D1 also concerns an autothermal reforming process, it uses exclusively catalysts containing one or more metals of the platinum group in this process and does not deal with the problem of soot formation or carbon deposition on the catalyst. For the preceding reasons, the board cannot accept the appellant's argument that D2 represents the closest prior art and considers this argument to be based on an hindsight analysis. It follows from the preceding considerations that D3 is closer to the claimed process than D2 or D1.

4. In the autothermal reforming process of D3 a part of the hydrocarbonaceous feed is subjected to a catalytic oxidation with oxygen in a first catalyst zone (24a) to produce a heated effluent suitable for steam reforming in the presence of a catalyst contained in a second catalyst zone (24b). The temperature attained within the first zone is high enough to catalytically steam reform gaseous hydrocarbons remaining in the first catalyst zone effluent without supplying external heat thereto (see Abstract; page 5, lines 4 to 27; page 6, lines 1 to 20; pages 38 to 44, Examples 3 and 4). In Example 3 a Pt-Rh reforming catalyst is used for the steam reforming reaction taking place in the second catalyst zone whereas in Example 4 the steam reforming catalyst is a commercially available nickel steam reforming catalyst (G9OC from United Catalysts, Inc.). According to page 43 of D3 a rapid increase in the reactor pressure drop was observed with the nickel catalyst of Example 4 and this could have been due to

soot accumulation on the nickel steam reforming catalyst.

4.1 Starting from this prior art, the technical problem underlying the claimed process can be seen in the provision of a process for the production of a gaseous mixture containing hydrogen, which avoids or at least reduces the soot formation on the nickel catalyst, in particular the growth of mechanically strong coal filaments, which causes the catalyst disintegration (see patent in suit, column 3 lines 30 to 50).

4.2 It is proposed to solve this problem by a process as defined in claim 1, which differs from the process of D3 in that it makes use of a nickel steam reforming catalyst in which at least 90% of the nickel particles (based on the number) are smaller than 10 nm. In view of the statement in column 3, lines 51 to 54, of the patent in suit and of the examples, in particular Examples 4 and 5 and comparative Example 5, it is credible that the problem stated above has actually been solved by the claimed process.

At the oral proceedings the appellant expressed doubts that the examples of the patent in suit supported claim 1 and the inventiveness thereof (see point V above). The appellant argued in this context that with a gas mixture containing 2 volumes of methane and one volume of oxygen as used in all the examples, no steam was produced in the oxidation step and thus, steam had to be added for the steam reforming reaction. This proposition is not convincing for the following reasons. According to the patent in suit, column 6, lines 9 to 23, oxygen incorporated by the oxidation catalyst can be used for carrying out the oxidation reaction that provides the necessary reaction heat. At a sufficiently high temperature, reduction of the metal oxide by the methane occurred rapidly. Thus, it can be inferred from the patent in suit that additional oxygen can be provided by the oxygen incorporated in the oxidation catalyst. Therefore, it appears that steam can be produced by the exothermic oxidation reaction even when the gas mixture contains 2 volumes of methane and one volume of oxygen. Concerning the appellant's second argument that the patent in suit contains no example with a catalyst having a nickel particle size within the preferred range, the board observes the following. It is disclosed in column 3, lines 51 to 58, that with a catalyst in which at least 90% of the nickel particles are smaller than 10 nm, carbon growth and disintegration of the catalyst do not occur. Therefore, use is made of a nickel catalyst whose Ni particles are <10 nm, preferably <5 nm, and more particularly <3 nm. In the examples of the patent in suit the catalyst has a nickel particle size falling within the definition of claim 1 (average size of 7.1 nm with no particles greater than 9 nm; or average size of 6.5 nm with no particles greater than about 8 nm). Although the exemplified catalysts do not have a particle size falling within the preferred range of <5 nm or <3 nm, it is credible in view of the said statement in column 3, lines 51 to 58, and in the absence of evidence to the contrary, that the problem stated above has been solved by the claimed process on the whole range defined in claim 1 for the nickel particle size.

5. Neither D1 nor D3 contains information suggesting that the problem of carbon deposition on the nickel catalyst could be solved by using a steam reforming catalyst

having the claimed nickel particle-size characteristics in the autothermal reforming process. From page 43 of D3 it can be inferred that the use of a steam reforming catalyst containing a platinum group metal instead of nickel reduces the soot deposition. Therefore D3 would have pointed towards a different solution. In the autothermal reforming process of D1 a catalyst system comprising one or more compounds of metals of the platinum group is used (see pages 3 to 4, claims 1, 6). In the paragraph bridging pages 1 and 2 it is indicated that the catalysts commonly used for the conventional steam reforming processes are based on Ni supported on Al, Mg and Si oxides with high thermal stability; however the Ni particle size of these catalysts is not disclosed. Furthermore D1 does not deal with the problem of carbon deposition on the steam reforming catalyst.

6. D2 is a scientific article investigating the activity and stability of Ni/SiO_2 catalysts for steam reforming of methane at 565°C. The nickel catalysts were prepared by the Van Dillen's method. The starting materials and catalyst preparation are described on page 791 (see "Catalyst Preparation"). The nickel particle-size distribution of the resulting catalyst is not reported in D2. In the review of the prior art on page 791 (left-hand column), it is disclosed that the catalyst previously prepared by the Van Dillen's method (Van Dillen et al., 1976) has very small crystallites (1-2 nm particle size) and a narrow crystallite-size distribution. The latter is disclosed in D4. The question whether or not the catalysts prepared as described in D2 have a nickel crystallite-size distribution falling within the definition of claim 1 can remain open, since even if it were assumed to the

appellant's benefit that their nickel crystallite-size distribution meets the definition of claim 1, this would not change the outcome of the present decision.

The catalysts of D2 were tested in the steam reforming of methane at 565°C at a very high steam/methane ratio (hereinafter R) of 5.7 and at a lower ratio of 2.3. At R=5.7 the catalyst deactivated very rapidly and permanently. As pointed out by the appellant, such a R value of 5.7 is normally not used in an industrial steam reforming process. However, the skilled person would have inferred from the overall teaching of D2 that the catalyst deactivates not only at R=5.7 but is also likely to at high R values (see page 790, summary; page 795, right-hand column, lines 8 to 21). Concerning the steam reforming reaction performed at a R value of 2.3, D2 teaches that the catalysts were stable and no deactivation occurred during a reaction period of 5 hours. Once the reaction was stopped, however, the catalyst activity could not be regained (see page 792, left-hand column, paragraph headed "Activity and Stability"; right-hand column, lines 1 to 3, Figure 3; page 794, paragraph bridging the two columns). As pointed out by the respondent, the fact that the catalyst activity cannot be regained once the reaction is stopped represents a drawback in an industrial process since the latter has to be stopped for maintenance, or for replacing part of the catalyst or for unscheduled reasons, and then the whole catalyst has to be replaced. Furthermore D2 is silent as to whether or not carbon deposition occurred on the surface of the catalyst at this lower R value. The problem of carbon deposition on the surface of the catalyst and solutions for reducing carbon deposition are in fact not discussed in D2. It is merely stated in connection with the catalyst deactivated at a high R value that the deactivation was not the result of a carbon overlayer: see the comments on the XPS results (X-ray photoelectron spectroscopy) on page 794, right-hand column, 4th paragraph). It is clear from D2 that this teaching concerns the deactivated catalyst and not the catalyst used at a R value of 2.3 for which no deactivation occurred within the 5 hour period of testing. Furthermore the catalyst of D2 was tested in a conventional methane-steam reforming process and not in an autothermal reforming process involving combustion of a part of the methane with oxygen. According to the patent in suit, the prevention of soot formation is cumbersome in such a process (see column 3, lines 8 to 16). In addition, the steam reforming reaction was carried out for a relatively short period of only 5 hours at R=2.3 and D2 does not suggest that carbon deposition might be avoided or reduced at this low R value by using a catalyst having a small nickel crystallite size and a narrow size distribution. For all the preceding reasons the teaching of D2 would not have given the skilled person an incentive to try the catalyst of D2 in the autothermal reforming process of D3 (or D1) in order to solve the problem stated above. In view of the teaching of D2 he could not have expected that the catalyst disclosed therein might solve this problem. In the board's judgement, the appellant's conclusions concerning the lack of inventive step are therefore based on an hindsight analysis of D2.

7. D4 was cited by the appellant only to show that the catalysts of D2 have a nickel particle-size distribution falling within the definition of claim 1. This document does not deal with the problem of carbon

deposition on the surface of this nickel catalyst in an autothermal steam reforming process and contain no information as to how this problem might be solved.

8. D5 was cited by the appellant in the grounds of appeal as a direct reply to the reasons given in the appealed decision. It discloses no additional information which, in combination with the teaching of D1 to D4, would point towards the claimed process to solve the technical problem stated above. This document deals with the problem of resistance to coking of nickel catalysts for the steam reforming of hydrocarbons, in particular with their resistance to carbon deposition in the steam reforming of n-butane. According to D5 the resistance to coking of the examined nickel catalysts in the steam reforming reaction is determined by two parameters, namely (a) the quantitative ratio of the Ni phase and the NiO+MgO mixture and (b) the chemical composition of the NiO+MgO mixture. D5 does not disclose the Ni particle-size distribution but only the mean size of the Ni crystallites. In the appellant's view, it was known from D5 that the deposition of carbon on the reforming catalyst could be avoided by using a Ni catalyst having a mean size d_H of the nickel crystallites of less than 10 nm and that the carbon deposition was more important, the greater the mean size. These arguments cannot be accepted by the board for the following reasons. They are based on the data reported on Figure 3 and in Table 1; however they are not confirmed by the data of Figure 2 which relates to the catalysts reduced at 973K and shows that the catalysts having lower d_H lead to higher coking rates. Comparison of catalyst B reduced at 973K with catalyst E (see Table 1 and Figure 9) further shows that the catalyst having the higher d_H has a better coking

resistance. The appellant's conclusion drawn from Figure 3 and Table 1 is neither in agreement with Figures 2 and 9 nor with the whole teaching of D5 according to which the resistance to coking of the analysed catalysts in the hydrocarbon steam reforming reaction is determined by the two parameters (a) and (b) indicated above. Therefore, D5 would rather point towards another direction as regards the factors influencing the carbon deposition and it would not have given suggestion towards the claimed solution even in combination with the other cited documents.

9. It follows from the above that the subject-matter of claim 1 meets the requirements of inventive step set out in Articles 52(1) and 56 EPC.

10. Claim 1 being allowable, the same applies to dependent claims 2 to 14 whose patentability is supported by that of claim 1.

Order

For these reasons it is decided that:

The appeal is dismissed.

The Registrar: The Chairman:

U. Bultmann R. Spangenberg