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File Number: T 363/87 - 3.3.2

Application No.: 81 300 484.3

Publication No.: 0 034 444

Title of invention: Enhancement of zeolite catalytic activity

Classification: B01J 29/28

DECISION
of 6 February 1991

Proprietor of the patent: Mobil Oil Corporation

Opponent: Imperial Chemical Industries PLC

Headword: Steam activation/MOBIL OIL

EPC Articles 54 and 56

Keyword: "Novelty (yes) after amendment of claims"
"Inventive step (confirmed) - prior art leading away from the invention - non-obvious transposition"

Headnote

Case Number : T 363/87 - 3.3.2

DECISION
of the Technical Board of Appeal 3.3.2
of 6 February 1991

Appellant : (Proprietor of the patent)	Mobil Oil Corporation 150 East 42nd Street New York, New York 10017 (US)
Representative :	Cooper, John Anthony Carpmaels & Ransford 43 Bloomsbury Square London WC1A 2RA (GB)
Respondent : (Opponent)	Imperial Chemical Industries PLC Legal Department Patents P.O. Box 6, Bessemer Road Welwyn Garden City, Hertfordshire AL7 1HD (GB)
Representative :	Bryant, Tracey Imperial Chemical Industries PLC Legal Department: Patents P.O. Box 6, Bessemer Road Welwyn Garden City Hertfordshire AL7 1HD (GB)
Decision under appeal :	**Decision of Opposition Division of the European Patent Office dated 2 July 1987, posted on 17 August 1987, revoking European patent No. 0 034 444 pursuant to Article 102(1) EPC.**

Composition of the Board :

Chairman : P. Lançon
Members : M. Eberhard
R. Schulte

Summary of Facts and Submissions

I. European patent No. 0 034 444 was granted with twenty-six claims on the basis of European patent application No. 81 300 484.3.

II. The Respondent (Opponent) filed a notice of opposition, requesting revocation of the patent on the grounds of lack of novelty, lack of inventive step and insufficiency of disclosure. The opposition was supported, inter alia, by the following documents:

(1) US-A-4 016 218
(5) US-A-4 094 921
(6) US-A-3 980 586
(9) Journal of Catalysis, Vol. 60 (1979) pages 140-147.

The Respondent further relied upon (14) US-A-3 493 519 during the oral proceedings before the Board.

III. The Opposition Division revoked the patent on the ground that the subject-matter of Claim 1 of the main request was not novel and the subject-matter of Claim 1 of the subsidiary request lacked inventive step.

Claim 1 of the subsidiary request reads as follows:

"A method for increasing the catalytic activity, alpha, of a catalyst comprising an acid zeolite having a silica to alumina mole ratio of at least 12 and a constraint index within the range of 1 to 12, and a matrix material comprising clay, silica and/or a metal oxide, comprising contacting said zeolite with water vapour for a time t hours at a temperature T°K and a water vapour partial pressure P Pascals (Pa) so related that

$$0.01(Pt)_T < (P.t/101325) < 1.0(Pt)_T$$

where $(Pt)_T = 2.6 \times 10^{-9}e^{16000/T}$."

Claim 12 is directed to a process for hydrocarbon conversion which comprises contacting a hydrocarbon feedstock under conversion conditions with a catalyst comprising a zeolite whose activity has been increased according to this method.

As regards the subsidiary request the Opposition Division considered that the sole difference between document (9) and Claim 1 resided in providing a matrix for the zeolite catalyst. It would have been obvious to the skilled man faced with the problem of providing an active hydrocarbon conversion catalyst on a large scale to incorporate a matrix material as support and extender for the zeolite. This measure was extremely well-known in the art and was exemplified by many of the cited documents. According to the decision, the use of such matrices was also suggested in document (6) in the context of zeolite activation.

IV. The Appellant lodged an appeal against this decision. An affidavit of the inventor was filed in addition to the statement of grounds of appeal. Oral proceedings were held on 6 February 1991. During these proceedings the Appellant handed over an amended Claim 1 as single request. This claim differs from Claim 1 reported hereabove in that the terms "comprising contacting said zeolite with..." have been replaced by "consisting of contacting said catalyst with...".

V. In support of his request, the Appellant argued essentially as follows:

It was the basic assumption in the state of the art that hydrothermal treatment of zeolites tends to bring out loss of crystallinity and therefore also of structure-determined properties such as catalytic activity. Enhancement of activity by steaming is a new phenomenon, quite independently of the means of its achievement. The fundamental assumption which persists throughout the entire text of (9) is that deactivation of the ZSM-5 occurs. Since the high α-values of Table 3 directly contradict the consistent teaching of (9) regarding the deactivation effect of steam of zeolites, the skilled man seeking to check the data of Table 3 would turn first to the matter of activation energy because the authors confess the potential unrealiability of their selection of the value 30 kcal/mole. If the calculation is performed on the basis of the true averaged activation energy of 15 kcal/mole, the α-value is found to be 249 for the HZSM-5 (120) instead of 7600. As the initial alpha values of the unsteamed zeolites are not disclosed, it cannot be assessed from Table 3 whether activation has actually occurred. The initial α-value depends not only on the SiO_2/Al_2O_3 mole ratio but also on the method of preparation and the subsequent treatments of the zeolite which are not clearly defined in (9). Samples of unsteamed HZSM-5 of approximately 120 SiO_2/Al_2O_3 mole ratio have been observed to manifest α-values higher than 249. Even if activation did occur in (9), this occurrence went unrecognised and unreported.

In document (5) the steam treatment of the zeolite is effected in order to reduce the α-value thereof. In the specific examples, in particular runs 4 and 5 of Table 1, the conversion of toluene is indeed higher after a steam treatment of one hour but the conversion of ethylene is less. A comparison of runs 5 to 9 shows that better results are obtained as regards the ethyltoluene selectivity under more severe steaming conditions. Therefore the skilled person reading (5) would be led in another direction.

The improvement in catalytic performance disclosed in (6) results from a treatment including silylating, calcinating and steaming. In Example 3 the conditions of the steam treatment lie outside the claimed range and from the comparison of examples 3 and 4 of Table III, it can be concluded that the steam treatment alone leads to a decrease in activity of the unmodified NH_4Y zeolite.

The main aim of document (14) is to improve the hydrothermal stability of Y zeolites. This problem does not exist in the case of the ZSM-5 zeolites since they are much more stable than the Y ones. Therefore the teaching of (14) would be useless for the skilled person. Furthermore, taking into account the fundamental differences between these two kinds of catalysts (i.e. different constraint index, SiO_2/Al_2O_3 ratio, steam stability, etc.), an activation effect of the ZSM-5 could not be expected in view of the teaching of (14).

VI. The main arguments put forward by the Respondent can be summarised as follows:

The subject-matter of Claim 1 is not novel over the disclosure of document (9). As it is extremely well-known in the art to incorporate a matrix to a zeolite, treatment of the composited zeolite would be implicit to the skilled man reading (9). Furthermore, the data in Table 3 is a clear teaching that a steam treatment of zeolite ZSM-5 under conditions conforming to the relationships set out in Claim 1 leads to activation of this zeolite. Although the initial alpha values of the zeolites are not mentioned in (9) it is known from Journal of Catalysis 61 (1980), page 393, Fig. 2 that the α-activity of an HZSM-5 zeolite having a SiO_2/Al_2O_3 ratio of 120 is about 70. Thus even if the α-values stated in Table 3 of (9) were based upon a false assumption as regards the activation energy, the corrected alpha value of 249 proposed by the Appellant using an activation energy of 15 kcal/mole would however indicate that an activation of the zeolite has occurred.

Assuming that the claimed process is new, then it lacks an inventive step over the disclosure of document (5) or document (6). The conditions of the steam treatment used in example 1 of document (6) correspond to the claimed one. The starting material is not a zeolite however the steaming conditions mentioned in column 5 are described for all the materials embraced by this document, including ZSM-5. These steaming conditions also lie within the scope of the claimed treatment. The treated materials of (6) are stated to be more catalytically active and zeolite ZSM-5 is clearly included among these materials.

The conditions for steam treatment given in column 11 of document (5) conform at a wide range of temperatures to those set out in Claim 1. Moreover, it is shown in Table 1, runs 4 and 5, that an HZSM-5 zeolite which has been steamed one hour gives a better toluene conversion than an unsteamed zeolite and therefore exhibits a higher α-activity. The ethyltoluene selectivity of run 5 is also higher than that obtained in run 4.

Document (14) which is a patent of the Appellant is cited in order to refute the Appellant's contention that the effect of steaming to enhance the activity of zeolites is a new phenomena.

The requirements of sufficiency of disclosure are not met if, as contended by the Appellant, document (9) teaches that steaming deactivates zeolite HZSM-5 since Claim 1 fails to identify any features over and above those disclosed in (9) which account for the activation observed.

VII. The Appellant requests that the decision under appeal be set aside and that the patent be maintained on the basis of Claim 1 filed during oral proceedings and Claims 2-26 as granted with the amendments in Claim 11 received on 21 February 1986.

The Respondent requests that the appeal be dismissed.

Reasons for the Decision

1. The appeal is admissible.

2. There are no objections under Article 123(2) and (3) to the amended Claim 1. The claimed relationship between P, t and T is supported by Claim 16 of the application as originally filed. Although it is indicated on page 19, lines 20-27, that "for only small size zeolites, the preferred range is also applicable", it is clear from the statement in lines 20-23 of the same page that the preferred range applies to both the large crystal size zeolites and the small crystal size zeolites. Furthermore, the application as originally filed also illustrates the treatment of large crystal size zeolites under conditions which fall within the preferred and narrower relationship (cf. examples 5 and 6). The steam treatment of the catalyst, i.e. of both the zeolite and the matrix material comprising clay, silica and/or a metal oxide, is based on page 15, lines 6-12 of the original application, it is further illustrated in example 2. There is also support for the replacement of the term "comprising" by

"consisting of" in particular at page 3, lines 21-25 of the application and in all the examples. In addition, the amended Claim 1 manifestly does not broaden the scope of the granted Claim 1.

3. After examination of the cited documents, the Board has come to the conclusion that none of them discloses enhancing the catalytic activity alpha of a catalyst comprising a matrix and a zeolite as defined in Claim 1 by steaming the catalyst under the controlled conditions recited in this claim.

3.1 The conditions of the steam treatment stated on page 142 of document (9) (cf. right-hand column, the two last sentences) fall within the limits set out in Claim 1. Furthermore, ZSM-5 in the ammonium form, which was steamed under these conditions, corresponds to the general definition of the zeolite given in Claim 1, when construed as indicated at page 7, lines 9-11, of the patent in suit (see also the dependent Claims 2 and 4). However, document (9) discloses neither the effect of this specific steam treatment on the zeolites nor the α-values of the **unsteamed** zeolites which would permit by comparison with the α-values reported in Table 3 to conclude whether or not the zeolites have undergone activation. In the Board's opinion, it cannot be **unambiguously** derived from the high α-values of Table 3 that activation of the ZSM-5 has actually occurred as a result of the steaming conditions. Thus, on the one hand, α-values of 7600 or >100 000 are not consistent with the fundamental asumption in (9) that steaming causes deactivation (cf. pages 145-146) and, on the other hand, the authors themselves draw attention to the potential unreliability of their selection of the value 30 kcal/mole for the calculation of the α-values and also mention possible values of from 15 up to 30 kcal/mole (cf. page 142, left-hand column, line 14 to right-hand column, line 5). Calculation of α-values based on a true averaged activation energy of 15 kcal/mole, which according to the Appellant may validly be used for the extrapolation of experimentation performed at 320°C, would lead to an α-value of about 249 for the steamed HZSM-5 (120) instead of 7600. This was not contested any longer by the Respondent during oral proceedings. However unsteamed HZSM-5 with a SiO_2/Al_2O_3 mole ratio of approximately 120 may exhibit very different α-values which depend upon the method of preparation and the subsequent treatment of the zeolite (for example ion-exchange, calcination). Alpha values of higher than 249 were mentioned by the Appellant whereas the Respondent referred to values of about 70 disclosed in Journal of Catalysis, Vol. 61, 1980 (page 393, Fig. 2). Under these circumstances, the Board comes to the conclusion that it is not implicit from the α-values of the steamed HZSM-5 (120) given in Table 3 that activation has occurred. This applies likewise to the α-values of the HZSM-5 (60) and HZSM-5(30). Furthermore document (9) does not disclose the steam treatment of the ZSM-5 zeolite composited with a matrix as defined in Claim 1.

It results from the preceding that the process of Claim 1 is novel over the disclosure of (9).

3.2 Since novelty of the claimed process with respect to the other cited documents is not in dispute and the Board has also reached the conclusion that their disclosure is not novelty-destroying, it is not necessary to consider this matter in detail.

4. It still remains to be examined whether the requirement of inventive step is met by the claimed subject-matter.

4.1 Document (9) was regarded as relevant to the claimed subject-matter when considering novelty in particular because of the accidental disclosure of steaming conditions which lie within the limits defined in Claim 1. However once novelty of the claimed process has been established this document does not, in the Board's view, represent the closest prior art since it consistently restates the known presumption that steaming reduces the activity of zeolites.

Document (6) relates to the improvement of the catalytic activity of materials suitable for hydrocarbon conversion (in particular catalytic cracking), such as silica-alumina, aluminosilicates or zeolites. This improvement is achieved by a three-step treatment, namely silylating, calcinating and steaming (cf. column 1, lines 48-53; column 3, lines 53-59; Claims 1-5). Although the process is exemplified with amorphous silica-alumina cracking catalysts and with a NH_4Y zeolite, other zeolites such as zeolites X, L, ZSM-4, ZSM-5, faujasite, erionite and mordenite can be treated in the same way (cf. Claim 5, column 2, line 39 to column 3, line 37). For use in hydrocarbon conversion, the treated zeolite is composited with a matrix material such as clay, silica and/or metal oxides (cf. column 6, lines 9-17). This document is considered to be the closest prior art.

4.2 In the light of this prior art, the technical problem underlying the patent can be seen in providing an alternative to this activation process which enables an increase in the catalytic activity **alpha** of catalysts containing a zeolite with a SiO_2/Al_2O_3 mole ratio of at least 12 and a constraint index within the range of 1-12, such as ZSM-5.

According to Claim 1 it is proposed to solve this problem by contacting the catalyst, which contains the zeolite in an acidic form and the matrix, with water vapour under operating conditions, i.e. temperature, water vapour partial pressure and time of contact, so related that they satisfy the formula given in Claim 1.

In view of the examples in the description and of Figure 1 which show that the catalytic activity alpha of the catalyst is increased by steaming under the relatively mild steaming conditions as defined in Claim 1 whereas more severe steaming conditions lead to a deactivation of the catalyst, the Board is satisfied that the technical problem has been plausibly solved.

4.3 As the Appellant himself admitted that the presence or the absence of the matrix may be presumed for the purposes of this appeal to have no influence on the attaining of the desired activation effect, the Board considers that this feature does not contribute in an inventive manner to the solution of the technical problem as stated above. Therefore the main question which arises as regards inventive step is whether or not the teaching of the cited documents suggests the treatment of the acid zeolite containing catalyst under the claimed steaming conditions in order to increase its alpha activity.

4.4 Document (6) discloses the steaming conditions of the silylated/calcinated material at column 5, lines 49-57, but does not mention the total pressure. From examples 1 and 2 in which the water vapour partial pressure is indicated, it can be derived that the α-activity of an amorphous silica-alumina catalyst is increased when it is subjected to successively a silylating step, a calcinating step and a steaming step under steaming conditions falling within the limits set out in Claim 1. However, on the one hand, the two first steps are necessary to obtain this improvement and, on the other hand, the treated catalyst is not a zeolite. Document (6) does not in any way suggest that the omission of the silylating and calcinating steps would lead to an increase in the α-activity of either an amorphous material or a zeolite. It should be noted in this context that the comparison of examples 3 to 6 which relate to NH_4Y zeolite rather points to the opposite direction. Thus they show that a NH_4Y zeolite modified by the three-step treatment does exhibit a substantial increase in cracking activity whereas the sole steam treatment carried out under the same steaming conditions leads to a decrease thereof (cf. Table III, conversion and rate constant). Therefore this teaching does not hint at the possibility of improving the α-activity of a catalyst containing a ZSM-5 zeolite by subjecting it to carefully controlled steaming conditions and, in the Board's view, it would have led the skilled person away from the claimed solution.

4.5 Document (5) is concerned with the selective ethylation of mono alkyl benzene in the presence of a catalyst comprising a matrix and a zeolite, such as ZSM-5, which has been subjected to a steam treatment within particular ranges of temperature, pressure and time (cf. Claims 14, 16 and 17; column 11, lines 3-12). However the aim of this steam treatment is to reduce the cracking activity alpha of the zeolite from an initial α-value of greater than 500 to less than 500, preferably between 0-20, in order to selectively produce the para or meta derivates of the mono alkyl benzene (cf. column 11, lines 3-15 and column 2, lines 11-19). This teaching would certainly not encourage the skilled person confronted with the opposite problem of increasing the α-activity of ZSM-5 containing catalysts to undertake further experimentation in connection with the steaming conditions.

The Board cannot follow the Respondent's arguments that in view of runs 4 and 5 in Table I, the skilled person would conclude to an improvement of the α-activity of the ZSM-5 by steaming. It is true that the toluene conversion is higher in run 5 than in run 4, however as pointed out by the Appellant the ethylene conversion has decreased so that no conclusion can be drawn as regards the α-value. In the Board's view the teaching of Table 1 is consistent with the rest of the description, namely that the steam treatment improves the selectivity of the catalyst.

4.6 The teaching of document (1) referred to in the decision under appeal is also that a steam treatment of zeolites such as ZSM-5 reduces their α-activity. Like document (6), this document cannot be helpful to the skilled person whose aim is, on the contrary, to increase the α-value of the catalyst.

4.7 Document (9) already discussed above in connection with novelty is consistent with the teaching of the preceding documents as regards the effect of steam on zeolites, in particular on ZSM-5. It clearly discloses the deactivation effect of steam on HZSM-5: see page 145, right-hand column, last sentence and page 146 left-hand column and Fig. 5. In view of this teaching and as the high α-values reported in Table 3 cannot be construed as resulting from an activation of the zeolite by steaming (see the reasons given above in point 3.1) the skilled person would not seek a solution to the problem of enhancement of the α-activity of a ZSM-5 containing catalyst in a steaming treatment thereof.

4.8 Document (14) was cited by the Respondent for the first time at a very late stage of the appeal procedure in order to refute the Appellant's contention that the effect of steaming to enhance the activity of zeolites is a new phenomena. In view of the fact that firstly this argument was itself put forward also for the first time at the appeal stage, secondly document (14) is a patent of the Appellant and thirdly it is of relevance for the present case, the Board has decided to take it into consideration (Art. 114(2)).

This document discloses a process for producing a hydrothermally stable Y zeolite of high hydrocarbon conversion activity which comprises calcining an NH_4Y zeolite in the presence of rapidly flowing steam under a water vapour pressure of at least 0.033 At and base exchanging the steamed product with an ammonium salt (cf. Claim 6). The tests carried out in example 2 demonstrate that the catalytic activity alpha increases and passes through a maximum as the humidity of the calcination atmosphere increases, the magnitude of this maximum depending upon the duration of the steam treatment (cf. column 5 and 6, example 2, table A and Fig. 1). The question which arises is whether in view of this teaching about NH_4Y the skilled person would have effected further experimentation as regards the steaming of a ZSM-5 containing catalyst in expectation of an increase in the alpha activity. In this respect the Appellant has argued that these two zeolites are fundamentally different as regards their constraint index, their SiO_2/Al_2O_3 mole ratio and also their properties, in particular their steam stability, so that the skilled person could not expect a similar activation effect by steaming. These arguments were not contested by the Respondent who, on his part, cited (14) only to show that activation of zeolites by steaming was known without contending that the teaching about NH_4Y would have been obviously transposable to ZSM-5. Furthermore documents (9), (5) and (1) all disclose a decrease in the α-value of ZSM-5 by steaming and the two curves illustrating the steam stability of HZSM-5 and HY in (9) (cf. page 146, Fig. 5) are so different from each other that the mechanisms of deactivation by steaming were supposed to be different. Under these circumstances the Board concurs with the Appellant's opinion that the skilled person aware of the fundamental differences between these two types of zeolites would not expect in view of the teaching of (9), (5), (1),(6) and (14) that steaming of ZSM-5 might lead to an activation thereof and therefore would not have been encouraged to carry out experimentation in this direction.

5. For the preceding reasons, the subject-matter of Claim 1 is considered to involve an inventive step. Claim 1 being allowable, the same applies to the dependent Claims 2-11 whose patentability is supported by that of Claim 1.

The Respondent has not raised any particular objection against the independent Claim 12 during the appeal procedure. This claim is construed by the Board as relating to a process for hydrocarbon conversion carried out in the presence of a catalyst activated by the method according to Claims 1 to 11, i.e. to the use of this catalyst in known hydrocarbon conversions. As this activated catalyst differs from the ZSM-5 zeolite of document (9) by the presence of the matrix, from that of (6) at least by a different surface structure and from the catalysts of (5) and (1) by a higher α-activity at comparable compositions, it is novel. Furthermore this improved α-activity was unexpected in view of the teaching of the cited documents about the deactivation effect of steam upon acid ZSM-5 zeolites. Under these circumstances the activated catalyst as such would be regarded as inventive. Therefore its use in known hydrocarbon conversions is also considered as patentable and Claims 12-26 are allowable.

6. The Respondent's contention that the requirements of sufficiency of disclosure are not met cannot be followed by the Board. Thus, firstly the Respondent has brought no evidence that the skilled person was unable to repeat the examples of the patent or that activation of the catalyst cannot be achieved when carrying out the invention as described in the examples. Secondly the Appellant has admitted that an activation of the zeolite may have occurred under the steaming conditions of NH_4 ZSM-5 disclosed at page 142 of (9). Therefore there exists no reason for believing that the disclosure of the invention is insufficient.

Order

for these reasons, it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the Opposition Division with the order to maintain the patent on the basis of Claim 1 filed during oral proceedings, Claims 2-26 as granted with the amendments in Claim 11 received on 21 February 1986 and an adapted description.

The Registrar: The Chairman:

M. Beer P. Lançon