

SPECIFICATION

PROCESS FOR PRODUCING LOWER OLEFINS

Field of the Invention

The present invention relates to a process for producing olefins which are lower than the raw materials from olefins having 4 to 12 carbon atoms, in particular ethylene and propylene by performing catalytic cracking using a catalyst.

Background of the Invention

Ethylene and propylene are important materials as basic materials for various chemicals and resins. Conventionally, although these olefins have been obtained by thermal or catalytic cracking in a naphtha cracker, the production ratio thereof is approximately 1:0.6 and this ratio becomes a cause of a difference in supply and demand between ethylene and propylene. Thus, in recent years, the process for selectively obtaining propylene from hydrocarbon raw materials including olefins having 4 to 12 carbon atoms such as butene and pentene, which are components having low value in use, is becoming increasingly important. There are many processes known for catalytically converting hydrocarbon raw materials including olefins having 4 to 12 carbon atoms by use of a zeolite catalyst. However, it has been

difficult to produce ethylene and propylene stably with high productivity for a long time by catalytically cracking hydrocarbon raw materials including olefins having 4 to 12 carbon atoms by use of a catalyst for the reasons given below.

For example, European Patent No. 109059 discloses a process for producing propylene by catalytically cracking butene by use of a proton type ZSM-5 zeolite (also referred to as an MFI zeolite). In this method, the reaction conditions such as low reaction temperatures of 400 and 500°C and a raw material feed rate per unit weight of catalyst (WHSV) of as high as 60 hr⁻¹ or more are used. However, since the concentration of the raw material butene used in this method is as high as 100% and the SiO₂/Al₂O₃ molar ratio of the zeolite catalyst is as low as 28, the production of cokes becomes large under these conditions - though there is no reference to this in the patent, and consequently the rate of decline in the activity of the catalyst becomes high. Therefore, it is not possible to use the process for a long time.

European Patent No. 109060 discloses a process for producing propylene by catalytically cracking butene by use of a proton type silicalite. Subsequent study has revealed that the silicalite used in this method is a zeolite having an MFI type zeolite structure. However, the concentration of the raw material butene used in this method is as high as 100%, and under the conditions of the high raw material feed rate per unit weight of catalyst (WHSV) at which high productivity can be achieved,

the rate of the decline in the activity of the catalyst is high. Besides, under the reaction conditions of the low temperature of 500°C which allows the catalyst to be used for a long time as described in Examples of the patent, the raw material feed rate per unit weight of catalyst (WHSV) is as low as 6 hr⁻¹, and consequently, the productivity in producing propylene and ethylene is low.

US Patent No. 5,981,819 discloses a process for producing propylene by use of a pentasil type zeolite in the presence of water in the olefin raw material under the conditions of the low reaction temperatures of 500°C or lower. However, in this process, the raw material feed rate per unit weight of catalyst (WHSV) is as low as 1 to 3 hr⁻¹, making it impossible to obtain high productivity in producing propylene and ethylene.

Japanese Patent Laid-Open No. 6-73382 discloses an example of the proton type ZSM-5. In an Example of the patent, it is stated that the reaction temperature was as high as 600°C to achieve high productivity on the assumption of a fluidized bed, and there was a precipitation of a large amount of cokes corresponding to 600 ppm relative to the total amount of the supplied raw materials. From this it can be predicted that when a fixed bed is used, the rate of the decline in the activity of the catalyst is high.

In the publications of Japanese Patent Laid-Open Nos. 11-246445 (corresponding to WO9929805), 11-246869

(corresponding to WO9929802), 11-246870 (corresponding to WO9929808), 11-246871 (WO9929804), 11-246872 (corresponding to WO9929806), 11-263983 (corresponding to WO9929807), 11-267510 (corresponding to WO9929421), 2001-26786 (corresponding to WO0077122), 2001-31979 (corresponding to WO0077123), 2001-31980 (corresponding to WO0100749), and 2001-40369 (corresponding to WO0078894) and European Patent No. 1195424, processes for producing a product containing ethylene and propylene by catalytically cracking hydrocarbon raw materials containing olefins by use of a proton type MFI zeolite are disclosed.

According to Examples described in the patents, in these processes, an MFI catalyst having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 360 or more was used, and the catalytic cracking reaction of butene proceeded without any fall in catalytic activity over a certain long period of time under the relatively gentle conditions of the reaction temperature of 550°C . However, in these processes, the raw material feed rate per unit weight of catalyst (WHSV) was as low as 30 hr^{-1} or lower, and as a result, high productivity was not obtained in the production of ethylene and propylene.

In addition, in this series of Patents, there is a reference to controlling the decline in the catalytic activity by reducing diene compounds in the raw material by means of hydrogenation, and there is also a reference to the statement that since the diene compounds cause a reduction in catalytic activity, it is preferable that the diene compound content of the raw material

be 0.1 wt% or less. For example, according to the description of the publication of Japanese Patent Laid-Open No. 11-246871 (corresponding to WO9929804), when the diene compound content of the raw material is 0.5 wt%, catalytic activity is not stable and the yield of propylene decreases with time (Comparative Example 4 in page 16 and Fig. 8 in page 38).

In the international patent WO0010948, there is a reference to the use of a ZSM-5 catalyst ion-exchanged with silver. In the process using such modified MFI catalyst, catalytic activity declines, and for this reason even if the reaction is performed at a little higher temperature of 600°C, the amount of precipitated cokes relative to the total amount of the supplied raw material is still large at 74 ppm by weight, for example, though the amount of precipitated cokes is reduced to some extent. Further, it is difficult in this process to carry out reaction under the conditions of a high raw material feed rate per unit weight of catalyst (WHSV), and therefore it is impossible to obtain high productivity in producing ethylene and propylene.

Specifically, under the conditions of higher reaction temperature, the formation of cokes is accelerated and catalytic activity falls. As a result, the raw material feed rate (WHSV) has to be reduced. On top of that, the yield of by-products, i.e., hydrogen, saturated hydrocarbons and aromatic hydrocarbons increases, and it is impossible to obtain high productivity in producing ethylene and propylene. On the other hand, as a result

of the modification, when a zeolite catalyst having lower activity is used or catalytic cracking reaction is performed under the conditions of lower temperature, the olefin raw material is not converted adequately, and the amount of unreacted raw material increases. As a consequence, the yield of ethylene and propylene falls, and high productivity cannot be obtained. Under such conditions, if an olefin having 4 to 12 carbon atoms as the raw material is supplied at a high rate (high WHSV) in order to achieve high productivity, the formation of cokes is accelerated instead, and as a result, the rate of the decline in catalytic activity becomes higher.

It is an object of the invention to provide a process for producing ethylene and propylene selectively with high productivity, in which, in producing lower olefins comprising ethylene and propylene as main components by catalytically cracking hydrocarbons containing olefins having 4 to 12 carbon atoms by use of a zeolite catalyst, the production of the by-products such as hydrogen, saturated hydrocarbon, aromatic hydrocarbon and cokes is controlled, the precipitation of cokes onto the catalyst is also controlled even when a raw material containing a relatively large amount of a diene compound is used, the extent of deterioration of the catalyst over a long time is small.

Disclosure of the Invention

The present inventors focused their efforts on a study to solve the problems as described above. As a result, the inventors have developed a production technology which shows high ethylene and propylene selectivity, low coke accumulation ensuring long catalyst life, and high productivity.

Such production technology has been successfully developed as a result of studying the mechanism of the catalytic cracking reaction which has not been systematically investigated until now. Specifically, the reaction mechanism for producing ethylene and propylene from olefins having 4 to 12 carbon atoms is significantly different between using the olefin (butene) having 4 carbon atoms and using olefins having more than 4 carbon atoms. That is, in the case of the olefins having more than 4 carbon atoms, carbocations are formed at acidic active sites of the catalyst and the carbon-carbon bond is broken, with the result that lower olefin is formed. On the other hand, in the case of butene, the mechanism can be explained as described below by reference to the isomerization reaction mechanism of olefins as reported in Applied Catalysis A: General 206 (2001) 57-66.

Specifically, in the case of butene, octene is first produced by dimerization thereof, and this octene forms a more stable secondary carbocation to finally turn into propylene and pentene. Since this reaction intermediate is stable, this reaction proceeds fast. Then, the pentene thus produced decomposes to form ethylene and propylene. However, since this

reaction proceeds via unstable primary carbocations for ethylene to be produced, the rate of this reaction is low. Further, the inventors of the present invention have made a study using the computational chemistry method, and as a result, they have obtained results which support the above assumption.

Specifically, there are a number of reactions involved in the reaction for obtaining propylene from butene. However, since the progress of such reactions differs, it is important for obtaining ethylene and propylene more selectively, to precisely control the reaction conditions such as catalytic activity, reaction temperature, and contact time to allow preferable reactions to proceed selectively.

In the present invention, a raw material containing at least one kind of olefin having 4 to 12 carbon atoms and 10 to 70 wt% of at least one kind of saturated hydrocarbon having 1 to 12 carbon atoms is caused to come into contact with a catalyst containing an MFI type zeolite catalyst at a raw material feed rate per unit weight of catalyst (WHSV) of 32 to 256 hr^{-1} at a reaction temperature of 400 to 580°C under a reaction pressure of 0.05 to 2 MPa, and the ratio by weight of pentene to propylene in the reaction product fluid is preferably controlled to 0.20 to 0.80. As a result, the production of by-products such as hydrogen, saturated hydrocarbon, aromatic hydrocarbon and cokes and the precipitation of cokes onto the catalyst are controlled even when a raw material containing a relatively large amount of a diene

compound is used, and therefore high selectivity and high productivity of ethylene and propylene and a long catalyst life is ensured.

Brief Explanation of the Drawings

Fig. 1 shows changes with time in the butene conversion and the yield of ethylene and propylene production in Examples 9, 10 and 1. The graph connecting rhombuses represents Example 9, the graph connecting squares represents Example 10, and the graph connecting circles represents Example 1. Further, the uppermost graph shows the conversion of butene, the middle graph shows the yield of propylene, and the lowermost graph shows the yield of ethylene.

Best Mode of the Invention

According to the present invention, ethylene and propylene can be selectively obtained mainly from the olefin components by catalytically cracking the raw material containing at least one kind of olefin having 4 to 12 carbon atoms and 10 to 70 wt% of at least one kind of saturated hydrocarbon having 1 to 12 carbon atoms by use of a catalyst. Surprisingly, the inventors of the present invention have found that by using such mixed raw material of olefins and saturated hydrocarbons, the production of cokes is controlled, and consequently the decline in catalytic activity is also controlled. Further, they have found that even

with the raw material containing a relatively large amount of a diene compound, the precipitation of cokes onto the catalyst is controlled, and consequently the decline in catalytic activity is also controlled. Further, even if the raw material contains hydrogen, the production of cokes can be controlled likewise. In this case, the partial pressure of hydrogen is preferably in a range of 0.1 to 0.9.

According to the invention, examples of the olefins having 4 to 12 carbon atoms in the raw material to be used include 1-butene, cis-2-butene, trans-2-butene, isobutene, 1-pentene, cis-2-pentene, trans-2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, cyclopentene, 1-hexene, 2-hexene, 3-hexene, methylbutenes, dimethylbutenes, neohexene, cyclohexene, methylcyclopentene, linear heptenes, branched heptenes, cyclic heptenes, methylcyclohexenes, and linear, branched or cyclic olefins having 9 to 12 carbon atoms.

According to the invention, the content of saturated hydrocarbons having 1 to 12 carbon atoms in the raw material to be used is 10 to 70 w%, preferably 10 to 60 wt%, and more preferably 20 to 50 wt%. Under the conditions of the invention, the conversion of such saturated hydrocarbons should not occur, but surprisingly, if the content of these saturated hydrocarbons in the raw material to be used is lower than the aforesaid range, the rate of the decline in catalytic activity becomes high. Examples of the saturated hydrocarbons having 1 to 12 carbon atoms

include methane, ethane, propane, n-butane, isobutane, linear, branched and cyclic pentane, linear, branched and cyclic hexane, linear, branched and cyclic heptane, linear, branched and cyclic octane. As components other than these, aromatic hydrocarbons such as benzene, toluene and xylene the like may be contained.

Further, according to the invention, the diene compounds contained in the raw material to be used are hydrocarbon dienes having 3 to 12 carbon atoms and may contain linear diene compounds such as propadiene, 1,2-butadiene, 1,3-butadiene, 1,2-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 2,3-pentadiene, 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2,3-hexadiene, 2,4-hexadiene, 1,2-heptadiene, 1,3-heptadiene, 1,4-heptadiene, 1,5-heptadiene, 1,6-heptadiene, 2,3-heptadiene, 2,4-heptadiene, 2,5-heptadiene, 3,4-heptadiene, 1,2-octadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, 2,3-octadiene, 2,4-octadiene, 2,5-octadiene, 2,6-octadiene, 3,4-octadiene, 3,5-octadiene and the like; branched diene compounds such as 2-methyl-1,3-butadiene, 3-methyl-1,2-butadiene, 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 3-ethyl-1,2-butadiene, 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, 2-methyl-1,4-pentadiene, 3-methyl-1,4-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 3,4-dimethyl-1,3-pentadiene, 2,3-dimethyl-1,4-pentadiene, 2,4-dimethyl-1,4-pentadiene,

2-methyl-1,3-hexadiene, 3-methyl-1,3-hexadiene, 4-methyl-1,3-hexadiene, 5-methyl-1,3-hexadiene, 2-methyl-1,4-hexadiene, 3-methyl-1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene and the like; and cyclic diene compounds such as cyclopentadiene, 1-methylcyclopenta-1,3-diene, 2-methylcyclopenta-1,3-diene, 5-methylcyclopenta-1,3-diene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene. However, since such components may cause an undesirable decline in catalytic activity, the content thereof is preferably 2 wt% or less, more preferably 1 wt% or less.

Examples of the raw material having such components include the fractions (raffinate-1) obtained by removing by extraction butadiene from the fractions (crude C4 distillate) which are obtained from the top of the debutanizer to which C1 to C3 fractions separated from a mixture obtained in a naphtha thermal cracker or in a naphtha catalytic cracker have been transferred, or an olefin fraction obtained by catalytically hydrogenating the total amount of the C4 fractions selectively without extracting butadiene from the crude C4 fractions so that the content of the diene component is 2 wt% or less, or the fractions (raffinate-2) obtained after separating isobutene from raffinate-1, or the fractions which are obtained from the bottom after removing by extraction isoprene from the fractions obtained from the bottom of the debutanizer (crude C5 fraction), or an olefin fraction obtained by catalytically hydrogenating the

total amount of the C5 fractions selectively without extracting butadiene from the crude C5 fractions so that the content of the diene component is 2 wt% or less, or the olefin fractions obtained by , or an olefin fraction obtained by catalytically hydrogenating selectively the total amount of the fractions which are obtained from the top of the depentanizer to which C1 to C3 fractions separated from a mixture obtained in a naphtha thermal cracker or in a naphtha catalytic cracker have been transferred without removing by extraction butadiene and isoprene from the aforesaid total amount of the fractions so that the content of the diene component is 2 wt% or less.

These raw materials may be used singly or in a mixture thereof formed in an arbitrary ratio. The raw materials are not limited to those as described above, any raw materials can be used as long as they contain olefins having 4 to 12 carbon atoms and 10 to 70 wt% of at least one kind of saturated hydrocarbon having 1 to 12 carbon atoms.

As for the catalyst used in the invention, an MFI type zeolite catalyst is employed. An $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the zeolite is usually from more than 120 to 5000 (inclusive), preferably from 200 to 5000, more preferably from 280 to 5000, and particularly preferably from 280 to 2000. If the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is less than those ranges, catalytic activity becomes too high. Thus, the precipitation rate of coke is high at the temperature range in which cracking reaction takes place

thermodynamically advantageously, and furthermore there is a problem in stability when the catalyst is repeatedly used. For this reason, such $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is not desirable. On the other hand, if the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is higher than this range, the number of the active sites decreases with the result that the catalyst cannot function as an acid catalyst no longer, and therefore such molar ratio is also undesirable.

For the MFI type zeolite catalyst, a commercially available product having an intended $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio may be used as it is, but it is possible to obtain it by using the methods known to the public in which zeolite having a composition falling outside these ranges is used as the raw material. In other words, it is also possible to convert a silica zeolite to a silica zeolite having a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio by means of the dealumination of a commercially available product having a low $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. Steam treatment, treatment with silicon tetrachloride, and treatment with hexafluorosilicate and other methods as described in, for example, *Catalysis and Zeolites, Fundamentals and Applications* (J. Weitkamp, L. Puppe Eds., Springer, 1999), pp. 127-155 can be quoted as examples of the dealumination method mentioned above.

Many of the commercially available products of the MFI type zeolite contain sodium or ammonium as cations, but any of them can be used in the invention as long as it is subjected to the treatment as described below. Specifically, a zeolite exchanged

with ammonium cations is treated at 500°C over 5 hours, for example, so that it is turned into the proton type, and then is used as a catalyst for catalytic cracking reaction. On the other hand, an MFI type zeolite having alkali metal ions such as sodium can be used after it is turned into the proton type by a method known to the public in which it is stirred at 60°C for 6 hours in an about 1 to 10% aqueous solution of ammonium nitrate, filtrated, washed and then treated at 500°C for 5 hours.

Since the aforementioned MFI type zeolite catalyst is required to be acidic, an acidic zeolite exchanged with metal ions, in addition to the proton type zeolite, can be used for the zeolite. Specific examples of the metal ions include IB group metals such as Cu and Ag as monovalent metal ions, and alkaline earth metals such as Mg, Ca, Sr and Ba, rare earth metals such as La and Ce and transition metals such as Fe, Ni, Mn, Co and V as polyvalent metal ions. These may be present at the same time in an arbitrary ratio with proton. In this case, all of the exchange capacity of zeolite may be replaced by the aforementioned proton or the aforementioned metals. However, if the activity is too high, part of the exchange capacity may be replaced by an alkali metal such as Li, Na, K or the like in an arbitrary ratio, so that acidity is lowered. However, if the ratio of the alkali metal in the exchange capacity exceeds 90%, acidity becomes too low, and therefore it is preferable to make the ratio no more than the range as described above.

For the MFI type zeolite, ones containing acidic elements such as P in addition to the ones as mentioned above can be used. In this case, the content of P is preferably no less than that of proton or other metal cations in terms of moles.

As a method for incorporating these elements into the catalyst, a method known to the public is employed. Examples of such methods include a method in which protons of the proton type MFI zeolite are exchanged with the cations of the metal atoms by ion-exchange method and a method in which a compound of the salt or complex of these elements is impregnated in the MFI zeolite.

For the MFI type zeolite catalyst, those which contain B, Sn, Ga, Mn, Fe and Ti as a tertiary metal other than Si and Al in the skeleton of the MFI type zeolite structure according to a method known to the public may also be used for the purpose of controlling activity, improving selectivity, controlling coke production and controlling the rate of the deterioration of the catalyst.

The MFI type zeolite catalyst can be subjected to steam treatment by a method known to the public before it is used. For the treatment method, preferably the temperature is 500 to 750°C, the steam pressure is 0.1 MPa to 1 MPa, and treatment time is 10 to 48 h. Further, the aforementioned treatment may also be performed after shaping the catalyst by a method as described below.

The aforementioned catalyst is filled into a reactor in any of the forms described below. Specifically, the MFI zeolite obtained by hydrothermal synthesis is essentially in a fine powder state. The fine powdered MFI zeolite catalyst thus obtained may be filled a fixed bed reactor as it is, but in order to prevent a pressure loss from increasing, it may be filled after it is physically mixed with a filler which is inert to the catalytic cracking, such as a silica ball or an alumina ball. Furthermore, the obtained fine powdered MFI zeolite catalyst may be mixed with a sintering agent (binder) which does not change the catalyst performance, and then be shaped. A representative example of the sintering agent is a silica system, but in addition to this, the sintering agent may be selected from among alumina-based, titania-based, zirconia-based and diatomaceous earth-based agents.

Sintering is preferably carried out in a range of 500 to 800°C. Further, examples of the form of shaped articles thus obtained include tablets, extrusions, pellets, spheres and microspheres, CDS extrusions, trilobes, guardlobes, rings, 2-spoke rings, special spoke rings such as HGS, EW and LDP, rib rings and granules.

According to the invention, catalytic cracking can be used in a reactor in any types such as a fixed bed reactor, a fluidized bed reactor and a moving bed reactor. However, the type of reactor is preferably a fixed bed reactor whose equipment is

simple. Catalytic cracking reaction is carried out by filling such reactor with the catalyst and supplying the hydrocarbon raw material containing olefins to the reactor. In conducting this catalytic cracking reaction, the reaction conditions are precisely controlled as described below.

Reaction temperature is set to be 400 to 580°C, preferably 480 to 580°C, and more preferably 480 to 560°C. Reaction temperature lower than those ranges is not desirable because the conversion of olefin supplied lowers at such lower reaction temperature and consequently sufficient productivity is not obtained in the production of ethylene and propylene. On the other hand, if the reaction temperature is higher than those ranges, the rate of the production of cokes accelerates, and the rate of the decline in catalytic activity becomes high.

Reaction pressure is set to be 0.05 MPa to 2 MPa, preferably 0.05 to 1 MPa, and more preferably 0.05 to 0.5 MPa.

The feed rate of the total raw materials per unit weight of the MFI catalyst (WHSV) is at least 32 to 256 hr⁻¹, preferably 40 to 256 hr⁻¹, and more preferably 40 to 128 hr⁻¹. If the feed rate of the raw materials (WHSV) is lower than those ranges, the pentene content of the resultant reaction product fractions becomes low, and furthermore the rate of the decline in catalytic activity is controlled to some extent. However, in this case, the yield of hydrogen, saturated hydrocarbon and aromatic hydrocarbon increases, and high selectivity and productivity in

the production of ethylene and propylene are not obtained. On the other hand, under the reaction conditions such as the raw material feed rate (WHSV) being higher than those ranges, the rate of the production of cokes becomes higher, and therefore such conditions are not preferable.

In addition, the reactor may be a single reactor or multiple reactors. In particular, in the case of multiple reactors, the reaction conditions can be controlled more precisely by installing reactors in series. Further, in the case of installing reactors in parallel, catalytic cracking operations are performed in one reactor while regeneration is carried out in another reactor. Switching the reactors for these operations makes it possible to maintain a constant production volume. Under such reaction conditions, maximum selectivity, yield and productivity of propylene are achieved, and the production of cokes which causes a fall in catalytic activity can be controlled.

According to the method of the invention, the weight ratio of pentene to propylene is set to be usually 0.20 to 0.80, preferably 0.25 to 0.80, and more preferably 0.30 to 0.80 in the reaction product fractions at the outlet of the reactor. Furthermore, in the case of installing multiple reactors in series, the weight ratio of pentene to propylene is set to be usually 0.20 to 0.80, preferably 0.25 to 0.80, and more preferably 0.30 to 0.80 in the reaction product fractions at the outlet of the first reactor.

In other words, in catalytic cracking reaction, a number of reactions whose rates are different proceed at the same time as described above, and the decomposition of pentene whose low reaction rate is lower than other reactions is controlled to some extent. This makes it possible to control undesirable accumulation of cokes and consequently to maintain constant catalytic activity for a sufficiently long time. In the case of removing ethylene and propylene from the product of the first reactor out of the multiple reactors installed, it becomes possible as a whole to convert most of the raw material supplied by carrying out the reaction in the second reactor under severer conditions.

On the other hand, in the case of using a single reactor alone, olefins having 4 or more carbon atoms including pentene are separated from the reaction product fractions and recycled to the catalytic cracking reactor so that they can be combined with a new raw material and used again. It is also possible to use these olefins having 4 or more carbon atoms in a naphtha cracker after they are separated and combined with a new naphtha raw material.

In the present invention, a raw material containing at least one kind of olefin having 4 to 12 carbon atoms and 10 to 70 wt% of at least one kind of saturated hydrocarbon having 1 to 12 carbon atoms is caused to come into contact with a catalyst containing an MFI type zeolite catalyst at a raw material feed rate per unit

weight of catalyst (WHSV) of 32 to 256 hr^{-1} at a reaction temperature of 400 to 580°C under a reaction pressure of 0.05 to 2 MPa, and the ratio by weight of pentene to propylene in the reaction product fluid is controlled to 0.20 to 0.80. As a result, the production of by-products such as hydrogen, saturated hydrocarbon, aromatic hydrocarbon and cokes and the precipitation of cokes onto the catalyst are controlled even when a raw material containing a relatively large amount of a diene compound is used, and therefore high selectivity and high productivity of ethylene and propylene and a long catalyst life is ensured.

The invention will be explained in greater detail below by using Examples, but the invention is not limited those Examples.

Example 1:

Commercially available powdery ammonium salt type ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 280) powder was calcined at 550°C over 5 hours. After calcination, compression shaping, crushing, and sieving were carried out to obtain a catalyst having a particle diameter of 250 to 500 μm .

For reaction, a fixed bed flow-through type reactor (inside diameter 10.7 mm, length 250 mm) was used. 0.125 g of the catalyst, and quartz sand and quartz wool as a support were filled in a quartz tube so that the total length becomes 250 mm. This quartz

tube was loaded in the reactor, the temperature of the catalytic bed was maintained at 550°C, the C4 fraction raw material C obtained by naphtha cracking (Table 1) was supplied at a flow rate of 8 g/hour and catalytic cracking reaction was performed under a reaction pressure of 0.05 MPa. The reaction product that flowed out was maintained in a gaseous state and was analyzed by means of gas chromatography.

After performing reaction for a predetermined time, the supply of the raw materials was stopped and the temperature of the catalytic bed was lowered to 450°C. After one hour from the stop of the supply of the raw material, the combustion of the accumulated cokes was started with air diluted with nitrogen. Until the combustion of the accumulated cokes was finished, the supply of air was continued. Hydrogen, carbon monoxide and carbon dioxide, which were formed through combustion reaction were analyzed by means of gas chromatography, and the weight of the produced cokes was calculated from the weight of these produced gases.

Conversion rate of the raw material and yield of the product were calculated by the following equations:

(1) Conversion of butene (%) = $(1 - (\text{weight of unreacted butene} / \text{weight of supplied butene})) \times 100$

(2) Yield of product (%) = $(\text{weight of each produced component} / \text{weight of supplied butene}) \times 100$

(3) Yield of cokes (PPM) = (total weight of produced

cokes/total weight of supplied butene) $\times 1,000,000$

The results of the reaction are shown in Table 2. The results indicate that over 90 hours, productivity of ethylene and propylene was obtained in a stable manner. Further, since the method in which the yield of the produced cokes was low and the cokes were removed by combustion, the amount of heat generated by the combustion of the cokes was small and the amount of undesirable vapor causing the deterioration of the catalyst was smaller. Therefore, it can be expected that as the catalyst is used repeatedly, its life gets longer.

Comparative Example 1:

Catalytic cracking reaction was performed under the same conditions as in Example 1, except that the raw material C of Example 1 were changed to n-butene raw material. The results are shown in Table 3. Under these conditions where the raw material containing no butane which is saturated hydrocarbon was used, the reaction time in which stable productivity of ethylene and propylene was obtained was only 20 hours.

Table 1

Composition of raw materials

	Raw material A	Raw material B	Raw material C	Raw material D	Raw material E
Components	wt%				
Saturated hydrocarbons					
Methane	0.1	0.0	0.0	0.0	0.0
Ethane	< 0.1	0.0	0.0	0.0	0.0
Propane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
iso-Butane	3.3	5.8	4.5	10.6	15.6
n-Butane	14.6	24.4	35.3	33.2	45.5
Pentane	0.2	0.3	0.2	0.1	0.1
Total for saturated hydrocarbons	18.4	30.6	40.0	43.9	61.2
Olefins					
trans-2-Butene	18.4	24.3	20.6	23.0	7.6
1-Butene	22.4	17.9	18.3	16.3	20.5
iso-Butene	12.3	13.1	0.3	3.2	3.6
cis-2-Butene	27.3	13.3	20.5	12.8	5.2
Total for butenes	80.4	68.6	59.6	55.3	36.9

Propylene	0.1	0.1	0.1	0.1	0.1
1,3-Butadiene	0.045	0.11	0.051	0.49	0.075
Others	1.2	0.7	0.3	0.3	1.8
Total	100.0	100.0	100.0	100.0	100.0

Table 2

Example 1

Reaction conditions	Catalyst H-ZSM-5 (SiO ₂ /Al ₂ O ₃ 280), Raw material C (Saturated hydrocarbons 40.0 wt%), temperature 550°C, WHSV 64 hr ⁻¹ , pressure 0.05 MPa									
Reaction time (hr)	4	12	20	30	42	54	66	78	84	90
Conversion of butene (%)	76.5	74.9	75.1	76.3	69.8	72.5	66.4	65.5	70.1	68.6
Yield (wt%)										
Hydrogen	0.10	0.08	0.11	0.09	0.06	0.05	0.05	0.03	0.04	0.05
Methane	0.43	0.33	0.48	0.41	0.28	0.24	0.23	0.18	0.26	0.28
Ethane	0.54	0.40	0.61	0.53	0.32	0.26	0.24	0.17	0.27	0.28
Propane	4.7	3.5	4.7	4.2	2.7	2.2	2.0	1.3	1.9	2.0
Butane	2.3	0.1	4.2	1.0	2.5	3.0	3.1	0.9	3.2	4.1
Ethylene	10.1	8.3	10.4	9.2	7.3	6.5	6.0	4.8	6.0	6.2
Propylene	31.4	30.7	33.2	30.5	32.0	30.0	31.3	28.9	29.5	32.2
Pentene	9.5	10.0	9.8	9.4	11.5	10.6	12.5	12.4	10.7	12.6

C5 or more non-aromatics	17.2	17.1	17.7	16.3	18.6	16.7	19.0	18.1	16.4	19.1
Aromatics	5.1	4.0	5.4	4.6	3.0	2.7	2.6	1.7	2.4	2.6
Coke	35 PPM									

Table 3

Comparative Example 1

Reaction conditions	Catalyst H-ZSM-5 (SiO ₂ /Al ₂ O ₃ 280), raw material n-butene, temperature 550°C, WHSV 64 hr ⁻¹ , pressure 0.05 MPa							
Reaction time (hr)	2	8	14	20	26	32	38	44
Conversion of butene (%)	79.1	78.0	74.5	68.6	57.4	41.6	26.3	14.5
Yield (wt%)								
Hydrogen	0.18	0.13	0.08	0.05	0.03	0.02	0.01	0.01
Methane	0.46	0.37	0.27	0.22	0.16	0.13	0.11	0.09
Ethane	0.45	0.37	0.26	0.18	0.09	0.06	0.04	0.03
Propane	4.2	3.3	2.4	1.6	0.75	0.30	0.11	0.04
Butane	6.3	5.3	4.5	3.9	2.8	2.0	1.3	0.8
Ethylene	10.3	8.9	7.5	5.8	3.3	1.6	0.7	0.3
Propylene	28.1	27.5	28.5	29.1	24.8	17.5	9.7	4.3
Pentene	8.8	9.1	10.6	12.2	12.7	10.6	6.9	3.5
C5 or more	16.6	15.7	16.7	17.5	16.1	12.4	7.8	3.8

non-aromatics								
Aromatics	7.1	5.7	4.4	3.3	1.9	1.0	0.47	0.18
Coke	103 PPM							

Examples 2 to 4:

Under the same conditions as in Example 1, except that in Examples 2 to 4, the raw materials as listed in Table 4 were respectively used, the raw materials containing 18.4 wt%, 30.6 wt% and 61.2 wt% of saturated hydrocarbons which were mainly butanes were subjected to catalytic cracking reaction. The results are shown in Table 4. As compared with Comparative Example 1, it can be seen that the yield of the produced coke was reduced by half and the reaction time in which stable productivity of ethylene and propylene was obtained lengthened sharply from 20 hours to 42 hours only because the raw material contained 18.4 wt% of saturated hydrocarbons. Example 4 is an example showing an example of the catalytic cracking of the raw material having the saturated hydrocarbon content of as high as 61.2 wt%. Although the operation was stopped after 100 hours from the start, the decline in catalytic activity at this point was low.

Table 4

Examples 1 to 4 and Comparative Example 1

	Comparative Example 1		Example 2		Example 3		Example 1		Example 4	
Reaction conditions	Catalyst H-ZSM-5 (SiO ₂ /Al ₂ O ₃ 280), temperature 550°C, WHSV 64 hr ⁻¹ , pressure 0.05 MPa									
Raw materials	Butene		A		B		C		E	
Saturated hydrocarbons (wt%)	0		18.4		30.6		40.0		61.2	
Reaction time (hr)	2	20	4	42	4	58	4	90	4	100
Conversion of butene (%)	79.1	68.6	77.1	68.5	77.0	66.4	76.5	68.6	77.0	72.8
Yield (wt%)										
Hydrogen	0.18	0.05	0.14	0.06	0.14	0.05	0.10	0.05	0.11	0.06
Methane	0.46	0.22	0.50	0.36	0.56	0.28	0.43	0.28	0.35	0.33
Ethane	0.45	0.18	0.55	0.39	0.68	0.26	0.54	0.28	0.50	0.44
Propane	4.2	1.6	5.2	2.1	5.3	1.9	4.7	2.0	4.6	3.8
Butane	6.3	3.9	5.0	2.1	3.3	1.7	2.3	4.1	1.7	1.3
Ethylene	10.3	5.8	10.1	6.4	11.1	6.2	10.1	6.2	9.1	8.9
Propylene	28.1	29.1	30.7	30.5	31.4	30.5	31.4	32.2	32.1	31.3
Pentene	8.8	12.2	9.5	12.5	9.2	11.9	9.5	12.6	9.2	10.4
C5 or more non-aromatics	16.6	17.5	16.5	17.6	17.2	18.0	17.2	19.1	18.6	18.1

Aromatics	7.1	3.3	6.6	3.5	6.8	3.0	5.1	2.6	4.2	3.4
Coke	103 PPM		57 PPM		52 PPM		35 PPM		26 PPM	

Examples 5 to 6 and Comparative Example 2:

Under the same conditions as in Example 1, except that in Examples 5 to 6 and Comparative Example 2, the reaction temperature was set to be 500°C, WHSV as listed in Table 5 was used and the raw material D was used, catalytic cracking reaction was performed. The results are shown in Table 5. As shown in Example 5, it can be seen that under the conditions where the raw material feed rate per unit weight of catalyst (WHSV) was as high as 128 hr⁻¹, the weight ratio of pentene to propylene was 0.5 or higher. Under these conditions, the production of the cokes was extremely small. However, as shown in Comparative Example 2, under the conditions of productivity being controlled, i.e., the value of WHSV being as low as 8 hr⁻¹, the yield of pentene decreased, but on the contrary, the yield of undesirable by-products such as saturated hydrocarbon, aromatic hydrocarbon and coke increased sharply.

Table 5

Examples 5 to 6 and Comparative Example 2

	Example 5	Example 6	Comparative Example 2
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Reaction conditions	Catalyst H-ZSM-5 (SiO ₂ /Al ₂ O ₃ 280), raw material D (saturated hydrocarbons 43.9 wt%), temperature 500°C, pressure 0.05 MPa					
WHSV (hr ⁻¹)	128		32		8	
Reaction time (hr)	7	43	7	43	8	44
Conversion of butene (%)	73.4	70.8	82.9	78.3	88.6	89.0
Yield (wt%)						
Hydrogen	0.04	0.03	0.14	0.11	0.42	0.33
Methane	0.10	0.06	0.36	0.31	1.4	1.2
Ethane	0.12	0.06	0.61	0.52	2.6	2.3
Propane	2.0	2.7	7.4	6.5	20.7	17.4
Butane	0.4	0.4	1.7	1.8	2.8	2.1
Butene	1.5	1.1	4.1	2.0	1.2	5.0
Ethylene	4.8	2.8	8.1	8.0	8.2	7.4
Propylene	25.6	22.7	21.0	24.8	15.9	14.9
Pentene	13.2	13.5	8.3	8.8	2.5	2.9
C5 or more non-aromatics	21.5	21.9	17.6	19.8	13.2	14.3
Aromatics	2.3	3.01	6.3	7.2	19.4	19.3
Cokes	11 PPM		33 PPM		120 PPM	

Example 7: Zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 500

Under the same conditions as in Example 1, except that in this Example, an MFI zeolite catalyst having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 500 was used, catalytic cracking reaction was performed for 137 hours. The results are shown in Table 6. Use of the zeolite having a high $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio made it possible to perform reaction 1.5 times or more than in Example 1 where the MF zeolite catalyst having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 280 was used, without any substantial decline in the productivity of ethylene and propylene.

Table 6

Example 7

Reaction conditions	Catalyst H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ 500), raw material C (saturated hydrocarbons 40.0 wt%), temperature 550°C, WHSV 64 hr^{-1} , pressure 0.05 MPa				
Reaction time (hr)	6	36	72	108	137
Conversion of butene (%)	75.1	77.9	72.1	70.3	67.7
Yield (wt%)					
Hydrogen	0.07	0.06	0.07	0.04	0.03
Methane	0.25	0.23	0.24	0.17	0.14

Ethane	0.31	0.24	0.21	0.17	0.19
Propane	3.8	3.5	2.5	2.0	2.3
Butane	0.9	2.5	1.0	2.3	1.4
Ethylene	11.7	11.1	8.4	9.0	7.9
Propylene	31.3	30.1	32.4	31.3	30.9
Pentene	11.6	12.2	10.5	12.0	12.7
C5 or more non-aromatics	16.7	18.5	17.4	19.3	19.3
Aromatics	4.4	3.2	3.7	2.4	2.8
Coke	32 PPM				

Example 8:

This Example represents an example of the repeated use of the catalyst. In Example 1, catalytic cracking reaction was performed, and the combustion of the produced cokes was carried out. The catalyst was held in the reactor, the raw material was supplied under the same conditions as in Example 1 to restart catalytic cracking reaction, and after reaction, the combustion of the produced cokes was performed under the same conditions. These operations were repeated 6 times, and as a result, deterioration of the catalyst was not observed at all.

Examples 9 and 10:

Under the same conditions as in Example 1, except that in

Examples 9 and 10, the raw material C having the butadiene content of 0.51 and 1.1 wt%, respectively, which was obtained by adding butadiene thereto, was used, catalytic cracking reaction was performed. The results are shown in Table 1. As compared with Example 1 in which the butadiene content was 0.05 wt%, the yield of propylene was obtained stably for 60 hours or longer even if the butadiene content was 1.1 wt%. Further, the yield of the produced cokes increased only slightly to 37 ppm and 40 ppm.

Claims

1. A process for producing olefins lower than the raw materials by catalytically cracking a hydrocarbon raw material including olefin by use of a catalyst, which is a process for producing ethylene and propylene which comprises catalytically cracking by use of a catalyst a hydrocarbon raw material which contains at least one kind of olefin having 4 to 12 carbon atoms and 10 to 70 wt% of at least one kind of saturated hydrocarbon having 1 to 12 carbon atoms at a raw material feed rate per unit weight of catalyst (WHSV) of 32 to 256 hr⁻¹ at a reaction temperature of 400 to 580°C under a reaction pressure of 0.05 to 2 MPa in the presence of a catalyst containing an MFI type zeolite catalyst, wherein the weight ratio of pentene to propylene which are contained in the reaction product fractions at the outlet of the reactor is 0.20 to 0.80.

2. A process as claimed in claim 1 for producing ethylene and propylene, wherein the SiO₂/Al₂O₃ molar ratio of the MFI type zeolite catalyst is from more than 120 to 5000.

3. A process as claimed in claim 1 or 2 for producing ethylene and propylene, wherein the content of saturated hydrocarbons having 1 to 12 carbon atoms in the raw material is 10 to 60 wt%.

4. A process as claimed in any of claims 1 – 3 for producing ethylene and propylene, wherein the reaction temperature of the catalytic cracking is 480 to 580°C.

5. A process as claimed in any of claims 1 – 3 for producing ethylene and propylene, wherein the feed rate of raw material per unit weight of catalyst (WHSV) is 40 to 256 hr⁻¹.

6. A process as claimed in any of claims 1 – 5 for producing ethylene and propylene, wherein at least one kind of olefin contained in the raw material is an olefin having 4 to 8 carbon atoms.

7. A process as claimed in any of claims 1 – 6 for producing ethylene and propylene, wherein the saturated hydrocarbons contained in the raw material are saturated hydrocarbons having 1 to 8 carbon atoms.

8. A process as claimed in any of claims 1 – 7 for producing ethylene and propylene, wherein 2 wt% or less of diene is contained in the raw material.