

## DESCRIPTION

## PROCESS FOR PRODUCING PROPYLENE

## 5 TECHNICAL FIELD

The present invention relates to a process for producing propylene from ethylene and methanol and/or dimethyl ether.

## 10 BACKGROUND ART

With respect to processes for the production of paraffins, olefins and aromatic hydrocarbons, various studies have been made not only on processes by cracking of petroleum but also on processes using, as raw  
15 materials, methanol and dimethyl ether obtained from a hydrogen/CO mixed gas obtainable by modifying natural gas as production processes wherein a new energy source is employed. Especially, in the latter processes, as compared with ones obtained by the former processes, the  
20 products contain substantially no sulfur compound and are thus expected to be prospective as environmentally-friendly petrochemical raw materials.

Such processes for producing paraffins, olefins and aromatic hydrocarbons by using methanol and dimethyl  
25 ether as raw materials, are usually named depending upon the types of the main products, i.e. a process to obtain gasoline as the main component is referred to as MTG

process, a process to obtain lower olefins as the main components is referred to as MTO process, and a process to obtain particularly propylene among the lower olefins, as the main component, is referred to as MTP process.

5        However, in a case where propylene is obtained from methanol (see e.g. Patent Documents 1 to 3), theoretically, one molecule of propylene will be formed from three molecules of methanol, whereby the yield based on the molar amount of the raw material methanol will be  
10        only 33% at the maximum. Besides, the weight of water to be formed as a by-product will be substantial. Accordingly, such a process can not be regarded to be preferable as an industrial process from the viewpoint of e.g. the efficiency of the installation costs.

15        On the other hand, as an embodiment of MTP process, a process is also known wherein propylene is obtained from ethylene and methanol (non-Patent Document 1). However, also by this process, the yield of propylene based on the raw material methanol did not exceed 40 mol%  
20        and was thus inadequate.

Patent Document 1: JP-A-59-222329

Patent Document 2: JP-A-4-217928

Patent Document 3: US-A-2003-139635

Non-Patent Document 1: Applied Catalysis A: General  
25        218 (2001), 241-250

## DISCLOSURE OF THE INVENTION

## OBJECT TO BE ACCOMPLISHED BY THE INVENTION

In the prior art, the yield of propylene based on the number of moles of the raw material methanol was low and inadequate as an industrial production process.

It is an object of the present invention to provide a process for producing propylene in a yield higher than the conventional process in the case where propylene is produced from ethylene and methanol.

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## MEANS TO ACCOMPLISH THE OBJECT

The present inventors have conducted an extensive study to accomplish the above object and as a result, have found that propylene can be obtained in high yield when ethylene is reacted with methanol and/or dimethyl ether under reaction conditions of specific ranges and have accomplished the present invention. Namely, the gist of the present invention resides in a process for producing propylene which comprises bringing ethylene in contact with methanol and/or dimethyl ether in the presence of a catalyst and which is characterized in that the amount of ethylene in a reaction mixture being discharged from the reaction system is reduced as compared with the amount of ethylene being fed to the reaction system, and that propylene is obtained in a yield of at least 40 mol% based on the sum of the number of moles of methanol and two times the number of moles of

dimethyl ether which are being fed to the reaction system.

In the process of the present invention, in order to increase the yield of propylene by reacting ethylene, it is preferred that the reaction pressure is adjusted within a range of at least 0.1 kPa and less than 2 MPa, and the amount of ethylene being fed to the reaction system is adjusted within a range of at least 1 and at most 20 by molar ratio based on the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system. Further, it is preferred that the weight hourly space velocity per weight of a catalytically active component, of the sum of methanol and dimethyl ether calculated as methanol, which are being fed to the reaction system, is adjusted within a range of at least 0.01 hr<sup>-1</sup> and at most 70 hr<sup>-1</sup>.

#### EFFECTS OF THE INVENTION

According to the present invention, using ethylene and methanol and/or dimethyl ether as raw materials, propylene can be produced in a yield higher than by the conventional processes.

#### BEST MODE FOR CARRYING OUT THE INVENTION

Now, a typical embodiment to carry out the present invention will be described in detail.

(1) REACTION SUBSTRATE (RAW MATERIAL)

The process of the present invention takes a form of gas phase reaction, and the raw material of the present invention is composed of a mixed gas comprising ethylene and methanol and/or dimethyl ether. This mixed gas may optionally contain, in addition to ethylene and methanol and/or dimethyl ether in a gas state, a gas inert to the reaction, such as helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, a paraffin, a hydrocarbon such as methane, an aromatic compound or a mixture thereof, for example, in an amount of from 1 mol% to 99 mol% as the concentration in the mixed gas. Among them, at least water (i.e. steam) is preferably co-existent.

Further, the mixed gas is not particularly limited with respect to the form in which it is being fed into the reactor so long as it is mixed at the time of the reaction. Ethylene and methanol and/or dimethyl ether, and further, if necessary, other gases inert to the reaction, may, respectively, be fed into the reactor, or they may preliminarily be made into a mixed gas, which may be fed into the reactor.

(1)-a ETHYLENE

The ethylene to be used in the present invention is not particularly limited, and one obtainable by various known methods may optionally be used, such as one produced from a petroleum-base material by e.g. a

catalytic cracking method or a steam cracking method, one obtainable by carrying out a FT (Fischer-Tropsch) reaction using as a raw material a hydrogen/CO mixed gas obtainable by gasification of coal, one obtainable by a  
5 dehydrogenation method or an oxidation dehydrogenation method of ethane, one obtainable by a methathesis reaction and homologation reaction of propylene, one obtainable from an oxygenated material of e.g. methanol and/or dimethyl ether by a catalytic reaction with a  
10 solid acid catalyst, or one obtainable by a dehydration reaction of the corresponding alcohol (ethanol). In such a case, one having a compound other than ethylene, attributable to the respective production method, mixed, may be used as it is, or purified ethylene may be used.

15       Among them, one using, as a raw material, ethylene produced from a petroleum-base material by e.g. a catalytic cracking method or a steam cracking method, is preferred. More preferred is ethylene obtained by using as a raw material a hydrocarbon having at least two  
20 carbon atoms and a boiling point of up to 300°C and having a sulfur content reduced by desulfurization, such as ethane, propane, a butane/butylene mixture, naphtha, light NGL, heavy NGL or kerosene light oil by catalytic cracking or steam cracking under such a condition that  
25 the outlet temperature of the cracking furnace would be from 760 to 900°C.

It is preferred to employ, as the ethylene, ethylene

obtained by an olefin production facility by thermal decomposition of naphtha, whereby in the olefin production facility, the yield balance of ethylene and propylene can be changed to substantially increase the  
5 propylene/ethylene ratio.

Further, it is preferred to use ethylene obtained by a lower olefin production facility from methanol and/or dimethyl ether, whereby in the lower olefin production facility, the yield balance of ethylene and propylene can  
10 be changed to substantially increase the propylene/ethylene ratio.

Still further, it is preferred to use ethylene obtained by an ethylene production facility by steam cracking of ethane, whereby propylene can be produced by  
15 using ethane separated mainly from natural gas, as the raw material.

Whereas, olefins obtainable by a method of thermal decomposition of naphtha which is commonly used as a method for producing olefins such as ethylene and  
20 propylene, usually contain about 28 wt% of ethylene, about 17 wt% of propylene and about 11 wt% of butene/butadiene on average, whereby there is a limit in changing the yield balance of ethylene and propylene depending upon the required balance of the two. Various  
25 thermal decomposition methods, etc. have been studied in this respect, but in either one of them, it is difficult to substantially change the yield balance. In the

process for producing a lower olefin such as ethylene, propylene or butene from methanol and/or dimethyl ether, as disclosed in the above mentioned Patent Document 3 or 4, for example, in Patent Document 3, a performance of about 50 wt% of propylene and about 20 wt% of butene, based on about 10 wt% of ethylene, is shown, and attention has been drawn as a process for selectively producing a lower olefin, but it is still difficult to substantially change the yield balance. Also in a process for producing ethylene by an ethylene production facility by steam cracking of ethane, although the composition of ethylene-containing products may differ depending upon the raw material composition, ethylene is mainly obtained, and it is difficult to obtain propylene.

Under these circumstances, the present invention provides a process which is useful for efficiently producing propylene from ethylene. Namely, the process for producing propylene of the present invention is an important technique which makes it possible to change the yield balance of ethylene and propylene in the above mentioned olefin production facility. Now, olefin production facilities (i), (ii) and (iii) will be described.

(i) Facility for the production of olefins by thermal decomposition of naphtha

As a facility for the production of olefins by thermal decomposition of naphtha in the present

invention, a steam cracking method will be described with reference to the flow of its outline. A steam cracking method is commonly used as a facility to produce olefins such as ethylene, propylene, etc. Its typical example is  
5 a tubular heating furnace process. In a front end methane-removal process as one method thereof, naphtha is introduced together with steam into a thermal decomposition furnace and thermally decomposed at a temperature of from about 760 to 900°C, whereupon  
10 hydrocarbons thereby obtained are quenched and then led to a fractionating column, whereby tar is obtained from the bottom of the column, a gas oil is obtained from the side of the column and hydrocarbons are obtained from the top fraction. The hydrocarbons as the top fraction are  
15 quenched for separation into hydrocarbons having mainly at most 5 carbon atoms and a mixture of water derived from steam and hydrocarbons having mainly at least 6 carbon atoms. The mixture of water and hydrocarbons having mainly at least 6 carbon atoms will be separated  
20 into water and hydrocarbons having mainly 6 carbon atoms. Further, the water separated here will be re-used via a steam generator as steam to be introduced into the thermal decomposition furnace. However, the separated water contains non-volatile hydrocarbons, and a part of  
25 the water will be disposed to remove such non-volatile hydrocarbons, and fresh water will be supplied to supplement the disposed water.

The hydrocarbons having mainly at most 5 carbon atoms obtained by quenching the top fraction will be compressed by a compressor, and then, a sulfur compound will be removed at an alkali-cleaning section, and after  
5 passing through a drying section, the decomposition product is led to a methane-removing column, whereby methane and hydrogen will be recovered as the top fraction. At the same time, the bottom fraction will be led to an ethane-removing column, whereby acetylene in  
10 the ethane-ethylene mixture as the top fraction will be converted by a hydrogenation reactor to ethane/ethylene which will be sent to an ethylene fractionating column, and at the same time, the bottom fraction will be led to a propane-removing column. Methylacetylene and  
15 propadiene in the propane/propylene mixture as the top fraction are converted by a hydrogenation reactor to propane/propylene, which is sent to a propylene fractionating column, and at the same time, the bottom fraction will be led to a butane-removing column. In the  
20 ethylene fractionating column, ethylene product is recovered from the side of the column, and ethane as the bottom fraction will be recycled to the decomposition furnace, and in the propylene fractionating column, propylene product is recovered from the side of the  
25 column, and at the same time, propane as the bottom fraction will be recycled to the decomposition furnace. By this system, ethylene of high purity at a level of

99.95% and propylene of high purity at a level of 99.0% will be separated and recovered.

Further, in a front end propane-removing process as another method, the decomposition product after passing  
5 through the drying section as described above, is led to a propane-removing column, whereby acetylene, methylacetylene and propadiene in the ethane/ethylene and propane/propylene mixtures as the top fraction are converted by a hydrogenation reactor to ethane/ethylene  
10 and propane/propylene, which will be led to a methane-removing column, and at the same time, the bottom fraction will be led to a butane removing column. In the methane removing column, methane and hydrogen will be recovered as the top fraction, and at the same time, the  
15 bottom fraction will be led to an ethane-removing column, whereby ethane/ethylene as the top fraction of the ethane-removing column will be sent to an ethylene fractionating column, and at the same time, the bottom fraction will be led to a propylene fractionating column.  
20 In the ethylene fractionating column, ethylene product will be recovered from the side of the column, and at the same time, ethane as the bottom fraction will be recycled to the decomposition furnace. Further, in the propylene fractionating column, propylene product will be recovered  
25 from the side of the column, and at the same time, propane as the bottom fraction will be recycled to the decomposition furnace.

Further, as another variation of the above mentioned front end propane-removing process, there is a method wherein the top fraction of the propane-removing column is led to an ethane-removing column i.e. not to the methane-removing column. In the top fraction of the propane-removing column, acetylene and methylacetylene are contained, and in a case where methylacetylene is contained in a large amount, it may be passed through the hydrogenation reactor in the same manner as mentioned above and then may be led to the ethane-removing column. Further, in a case where the methylacetylene content is small, it may be led to the ethane-removing column without passing it through the hydrogenation reactor, whereupon acetylene in methane, hydrogen and an ethane/ethylene mixture as the top fraction of the ethane-removing column may be passed through the hydrogenation reactor and converted to ethane/ethylene. The top fraction of the ethane-removing column may be passed through a hydrogen separator following the hydrogenation reactor installed as the case requires and then may be sent to the methane-removing column, and at the same time, the bottom fraction will be sent to a propylene fractionating column. In the methane-removing column, methane as the top fraction will be recovered, and at the same time, ethane/ethylene as the bottom fraction will be led to an ethylene fractionating column. In the propylene fractionating column, propylene product

is recovered from the side of the column, and at the same time, propane as the bottom fraction will be recycled to the decomposition furnace. In the ethylene fractionating column, ethylene product will be recovered from the side  
5 of the column, and at the same time, ethane as the bottom fraction will be recycled to the decomposition furnace.

Further, as still another method, a front end ethane-removing process is also available wherein the decomposition product after passing through the drying  
10 section as mentioned above, is led to an ethane-removing column.

In the present invention, it is preferred to produce propylene by reacting ethylene obtained by the above facility for the production of olefins by thermal  
15 decomposition of naphtha, with a gas containing methanol and/or dimethyl ether and to use water formed as a by-product, as a steam-generating source in the thermal decomposition of naphtha. It is thereby possible to reduce the cost for steam in the thermal decomposition of  
20 naphtha at the time of producing olefins by the thermal decomposition of naphtha.

As mentioned above, the heat decomposition furnace in the process for thermal decomposition of naphtha employs water as a diluting gas for naphtha, but a part  
25 of the recovered water is required to be disposed at the time of re-use. Further, depending upon the operation conditions of the heat decomposition furnace, water may

be deficient. Whereas, at the time of producing propylene from ethylene and methanol and/or dimethyl ether, 1 mol of water will be produced as a by-product per mole of methanol and/or dimethyl ether, and by such  
5 water formed as a by-product, it is possible to supplement water corresponding to the amount deficient in the steam-generating source.

Further, it is possible to utilize, for example, a part of water formed as a by-product at the time of  
10 producing propylene, as a diluting agent for ethylene and a gas comprising methanol and/or dimethyl ether in the reaction for producing propylene and to adopt a utilization method of e.g. supplying the remaining water to the steam-generating apparatus in the thermal  
15 decomposition of naphtha. Further, a part of water recovered from steam employed for the thermal decomposition of naphtha may be utilized as a diluting agent for ethylene and a gas comprising methanol and/or dimethyl ether in the reaction of ethylene with methanol  
20 and/or dimethyl ether.

Here, ethylene obtained by a facility for the production of olefins by thermal decomposition of naphtha is meant to include not only ethylene obtained via an ethylene fractionating column in the above front end  
25 methane-removing process, front end propane-removing process and front end ethane-removing process, but also an ethane/ethylene mixture after converting acetylene in

an ethane/ethylene mixture as the top fraction of the ethane removing column in the above front end methane-removing process to ethane/ethylene by a hydrogenation reactor, an ethane/ethylene mixture as the top fraction  
5 of the ethane-removing column in the above front end propane removing process, the mixture containing ethylene after converting acetylene in the methane, hydrogen and ethane/ethylene mixture as the top fraction of the ethane-removing column in the above mentioned another  
10 variation of the front end propane-removing process to ethane/ethylene by a hydrogenation reactor as the case requires, and the mixture containing ethylene after converting acetylene included in the methane, hydrogen and ethane/ethylene mixture as the top fraction of the  
15 ethane-removing column in the above front end ethane-removing process to ethane/ethylene by a hydrogenation reactor. Further, the mixture containing ethylene in the above mentioned another variation of the front end propane-removing process and the above mentioned front  
20 end ethane-removing process may also be one having at least a part of hydrogen and/or ethane contained in such a mixture is separated as the case requires.

Among them, it is preferred to employ an ethane/ethylene mixed gas obtainable from the top  
25 fraction of the above ethane-removing column as the ethylene obtained by a facility for the production of olefins by thermal decomposition of naphtha. It is

thereby possible to reduce the load in the ethylene fractionating column as compared with a case where ethylene product recovered from the side of the ethylene fractionating column is used as a raw material ethylene to be reacted with methanol and/or dimethyl ether. At the same time, ethane contained in an amount of from about 10 to 20% in the ethane/ethylene mixed gas will function as a carrier in the reaction with methanol and/or dimethyl ether, whereby it will be unnecessary to supply a carrier substance from outside, and the reaction of the ethylene with methanol and/or dimethyl ether can be carried out very efficiently.

Here, the ethane/ethylene mixed gas obtainable from the top fraction of the ethane-removing column is meant for one after converting acetylene in the ethane/ethylene mixture as the top fraction in the above front end methane-removing process to ethane/ethylene by a hydrogenation reactor, for ethane/ethylene as the top fraction in the above front end propane-removing process, for one after converting acetylene in the methane, hydrogen and ethane/ethylene mixture as the top fraction in the above mentioned another variation in the front end propane-removing process, to ethane/ethylene by a hydrogenation reactor as the case requires, or for one after converting acetylene included in the methane, hydrogen and ethane/ethylene mixture as the top fraction in the above front end ethane-removing process to

ethane/ethylene by a hydrogenation reactor.

Further, in the case of the mixture containing ethylene in the above mentioned another variation of the front end propane-removing process and in the above mentioned front end ethane-removing process, at least a part of hydrogen and/or methane contained in the mixture may be separated as the case requires. For example, in order to separate at least a part of methane after separation of hydrogen, a method may be mentioned wherein it is withdrawn from the side of the methane-removing column in such a process. Here, at the time of separating at least a part of methane, by leaving a part of methane, it is possible not only to reduce the load in the ethylene fractionating column as mentioned above but also to reduce the load in the methane-removing column. At the same time, not only ethane but also methane contained in the ethane/ethylene mixed gas will function as a carrier in the reaction with methanol and/or dimethyl ether and will thus help to efficiently carry out the reaction of ethylene with methanol and/or dimethyl ether.

(ii) Process for the production of lower olefins from methanol and/or dimethyl ether

A process for the production of lower olefins from methanol and/or dimethyl ether is a conventional process known by e.g. the above Patent Documents 1 to 4, and it is, for example, one to produce lower olefins such as

ethylene, propylene, butylene, etc., by reacting methanol and/or dimethyl ether at a temperature of from 200 to 600°C under a pressure of from 10 to 600 kPa in the presence of a solid acid catalyst or the like, if  
5 necessary, in the presence of water.

Here, the ratio of methanol and/or dimethyl ether to water is preferably 1:0 to 2. The solid acid catalyst as the catalyst is preferably a silicon-containing compound. The silicon-containing compound may, for example, be  
10 silicon dioxide, but is more preferably a crystalline aluminosilicate, a metasilicate or a crystalline aluminum phosphate, particularly preferably a zeolite. Further, the temperature is preferably from 300 to 600°C, and the pressure is preferably from 20 kPa to 1 MPa.

15 And, for example, methanol and/or dimethyl ether is reacted under the above described conditions, and the reaction gas is cooled, partially condensed and separated into three phases by a separator. Then, a liquid phase comprising higher fatty acids and aromatic compounds is  
20 taken out, and the rest being an aqueous phase and a gas phase, is washed with water in a washing column, and from its top, a gas mixture containing C<sub>2</sub>-C<sub>4</sub> olefins is taken out and separated into C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> by a known method, followed by purification to obtain ethylene product,  
25 propylene product and butylene product. On the other hand, from the bottom, an aqueous phase containing unreacted methanol and dimethyl ether as an unreacted and

intermediate product, is taken out, and from the aqueous phase, methanol and dimethyl ether are separated and recycled to the reactor, while water is removed.

As the separation/purification system for the gas mixture containing C<sub>2</sub>-C<sub>4</sub> olefins, for example, the gas mixture is passed through sequentially in the order of e.g. an ethylene/ethane-removing column, a methanol-removing column, a propylene/propane-removing column and a butylene/butane-removing column, and the ethylene/ethane mixture as the top fraction of the ethylene/ethane-removing column is, if necessary, subjected to such treatment that acetylene in the mixture is converted to ethylene/ethane by a hydrogenation reactor. Then, the mixture is sent to an ethylene fractionating column via a methanol-removing column, and at the same time, the bottom fraction is led to a propylene/propane-removing column, and the propylene/propane mixture as the top fraction of the propylene/propane-removing column is, if necessary, subjected to such treatment that methylacetylene and propadiene in the mixture are converted to propylene/propane by a hydrogenation reactor. Then, the mixture is sent to a propylene fractionating column, and at the same time, the bottom fraction is led to a butylene/butane-removing column. In the ethylene fractionating column, ethylene product is recovered from the top of the column, and ethane is separated from the

bottom of the column. Further, in the propylene fractionating column, propylene product is recovered from the top of the column, and propane is separated from the bottom of the column.

- 5        Here, ethylene obtained from the above mentioned facility for the production of lower olefins from methanol and/or dimethyl ether may, for example, be not only ethylene product recovered from the top of the ethylene fractionating column by subjecting an
- 10 ethylene/ethane mixture as the top fraction of the ethylene/ethane-removing column to such treatment that acetylene in the mixture is converted to ethylene/ethane by a hydrogenation reactor, as the case requires and then sending it to the ethylene fractionating column via a
- 15 methanol-removing column, but also an ethylene/ethane mixture as the top fraction of the ethylene/ethane-removing column, or the ethylene/ethane mixture after converting acetylene in the mixture to ethylene/ethane by the hydrogenation reactor, as the case requires.
- 20 (iii) Facility for the production of ethylene by steam cracking of ethane

      Steam cracking of ethane is a reaction wherein a mixture of alkanes containing mainly ethane is dehydrogenated, for example, at from 500 to 900°C under

25 at least atmospheric pressure, whereby mainly alkanes and partially dienes or alkynes, are obtainable. As a separation/purification system for the obtained reaction

mixture, for example, firstly a fraction heavier than C3 is separated in a front end type ethane-removing column, and a hydrocarbon mixture is recovered from the top of the column. Then, acetylene in the mixture is removed  
5 and converted to ethylene/ethane by a hydrogenation reactor, as the case requires. Thereafter, the mixture is sent to an ethylene fractionating column via a methane-removing column, and ethylene is recovered from the top of the column. Here, ethylene obtained by the  
10 facility for the production of ethylene by steam cracking of ethane to be used for the reaction of the present invention may be not only ethylene product recovered from the ethylene fractionating column, but also an ethylene/ethane/methane/hydrogen mixture as the top  
15 fraction of the methane-removing column, or a mixture after subjecting the column top mixture of the front end ethane-removing column to such treatment that acetylene in the mixture is converted to ethylene/ethane by a hydrogenation reactor as the case requires.

20 (1)-b METHANOL AND DIMETHYL ETHER

The production sources for methanol and dimethyl ether as raw materials are not particularly limited and may, for example, be coal or natural gas. Or, they may be ones obtainable by a hydrogenation reaction of a mixed  
25 gas of hydrogen/CO derived from a by-product in iron industry, ones obtainable by a modifying reaction of alcohols derived from plants, ones obtainable by a

fermentation method, or ones obtainable from organic substances such as recycled plastics or urban wastes.

Among them, a method of obtaining the above methanol and dimethyl ether by a hydrogenation reaction of a mixed  
5 gas of hydrogen/CO is preferred.

## (2) CATALYST

The catalyst to be used in the present invention is not particularly limited so long as it is a solid one having Bronsted acid sites. For example, a known  
10 catalyst may optionally be used such as a solid acid catalyst of e.g. a clay mineral such as kaolin; one having an acid such as sulfuric acid or phosphoric acid impregnated or supported on a carrier of e.g. clay mineral; an acid type ion exchange resin; an aluminum  
15 phosphate; a mesoporous silica alumina such as Al-MCM41; a zeolite; or a lamellar zeolite such as ITQ-2.

As the solid acid catalyst, one having a large surface area is preferred, and one having many acid sites is preferred. The BET specific surface area of a  
20 preferably employed solid acid catalyst is usually at least 100 m<sup>2</sup>/g, preferably at least 200 m<sup>2</sup>/g, more preferably at least 300 m<sup>2</sup>/g and usually at most 1,000 m<sup>2</sup>/g, preferably at most 800 m<sup>2</sup>/g, more preferably at most 700 m<sup>2</sup>/g. Further, the pore volume is usually at  
25 least 0.01 cc/g, preferably at least 0.05 cc/g, more preferably at least 0.1 cc/g and usually at most 0.8 cc/g, preferably at most 0.6 cc/g, more preferably at

most 0.5 cc/g.

Among such solid acid catalysts, one with acid strength being not so high is preferred. For example, mesoporous silica, zeolite or lamellar zeolite may be  
5 mentioned.

(i) ZEOLITE

The structure of the zeolite may, for example, be, as represented by the codes stipulated by International Zeolite Association (IZA), AEI, AET, AEL, AFI, AFO, AFS,  
10 AST, ATN, BEA, CAN, CHA, DDR, EMT, ERI, EUO, FAU, FER, LEV, LTL, MAZ, MEL, MFI, MOR, MTT, MTW, MWW, OFF, PAU, RHO, STT, TON, etc.

Among them, one having micropores having a pore diameter of from 3 to 9 Å is preferred.

15 Among zeolites, a crystalline porous silicate or a crystalline porous aluminophosphate is preferred, and a crystalline porous silicate modified with a metal element of Group 1 to 14 of the Periodic Table other than silicon and aluminum elements, or a crystalline porous  
20 aluminophosphate similarly modified is more preferred.

(i)-a CRYSTALLINE POROUS SILICATE

The crystalline porous silicate may, for example, be a crystalline porous silicate, aluminosilicate, aluminophosphosilicate, borosilicate, aluminoborosilicate  
25 having a part of silicon elements substituted by an aluminum element and/or a phosphorus element and/or a boron element, or a metal silicate having a part of

silicon elements substituted by another element. Among them, a silicate, an aluminosilicate, an aluminophosphosilicate, a crystalline aluminosilicate substituted by an aluminoborosilicate, or the after-  
 5 mentioned modified crystalline porous silicate, is preferred. Further, the aluminosilicate is preferably one having a molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  being larger than 10.

The structure of such a crystalline porous silicate  
 10 may, for example, be, as represented by the codes for zeolites stipulated by International Zeolite Association (IZA), AEI, AET, AEl, AFI, AFO, AFS, AST, ATN, BEA, CAN, CHA, DDR, EMT, ERI, EUO, FAU, FER, LEV, LTL, MAZ, MEL, MFI, MOR, MTT, MTW, MWW, OFF, PAU, RHO, STT, TON, etc.  
 15 And AFI, BEA, CAN, CHA, DDR, EMT, ERI, EUO, FAU, FER, LEV, LTL, MAZ, MEL, MFI, MOR, MTT, MTW, MWW, OFF, PAU, RHO, STT and TON are preferred. Specifically, SSZ-24, etc. having a AFI structure,  $\beta$ , etc. having a BEA structure, Cancrinite, etc. having a CAN structure,  
 20 Chabazite, SSZ-13, etc. having a CHA structure, sigma-1, etc. having a DDR structure, EMC-2, etc. having a EMT structure, Erionite, etc. having an ERI structure, EU-1, etc. having an EUO structure, USY, etc. having a FAU structure, Ferrierite, ZSM35, etc. having a FER  
 25 structure, Levyne, etc. having a LEV structure, L-type zeolite, etc. having a LTL structure, Mazzite, etc. having a MAZ structure, ZSM5, etc. having a MFI

structure, ZSM11, etc. having a MEL structure, Mordenite, etc. having a MOR structure, ZSM23, etc. having a MTT structure, ZSM12, etc. having a MTW structure, MCM22, etc. having a MWW structure, Offrertite, etc. having an  
5 OFF structure, ECR18, etc. having a PAU structure, Rho, etc. having a RHO structure, SSZ23, etc. having a STT structure, and ZSM22, etc. having a TON structure, may be mentioned. Among them, preferred are ones having an AEI structure, a BEA structure, a CHA structure and a MFI  
10 structure, and particularly preferred are ones having a BEA structure and a MFI structure. Specifically,  $\beta$  and ZSM5 may, for example, be mentioned.

They may be various commercial products. Otherwise, those synthesized by a known method disclosed, for  
15 example, in "Verified Syntheses Of Zeolitic Materials" (2<sup>nd</sup> Revised Edition 2001 Elsevier) published by IZA, may be employed.

Further, among the above crystalline porous silicates, a crystalline porous aluminosilicate having an  
20 aluminum element may be one wherein a part of aluminum atoms constituting the crystalline porous silicate containing an aluminum element is subjected to removal of aluminum by e.g. steaming or acid treatment to have a high silica/alumina ratio. It is particularly preferably  
25 one having a molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  being at least 30, more preferably at least 50, further preferably at least 100, particularly preferably at least 200. On the other

hand, as its upper limit, the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio is usually at most 1,000, more preferably at most 750, particularly preferably at most 500. With ZSM5, etc., the Al content can be adjusted not only by the above  
5 method but also by controlling the Al amount at the time of its synthesis.

The crystalline aluminosilicate is preferably one having a BET specific surface area of from  $200 \text{ m}^2/\text{g}$  to  $700 \text{ m}^2/\text{g}$  and a pore volume of from  $0.1 \text{ cc/g}$  to  $0.5 \text{ cc/g}$ .

10 (i)-b CRYSTALLINE POROUS ALUMINOPHOSPHATE

The crystalline porous aluminophosphate may be one having aluminum elements and phosphorus elements constituting it are partly substituted by silicon elements and/or boron elements, such as a crystalline  
15 porous aluminophosphate, silicoaluminophosphate or boroaluminophosphate, and it may further be one substituted by other metal atoms or the after-mentioned modified crystalline porous aluminophosphate.

The structure of such crystalline porous  
20 aluminophosphates may, for example, be, as represented by codes for zeolites stipulated by the above mentioned IZA, AEI, AEL, AFI, AFO, AST, CHA, ERI or FAU. Preferred is CHA.

The above crystalline porous aluminophosphate is  
25 preferably a crystalline porous silicoaluminophosphate. Specifically, SAPO18, etc. having an AEI structure, SAPO5, etc. having an AFI structure, SAPO41, etc. having

an AFO structure, SAPO11, etc. having an AEL structure, SAPO16, etc. having an AST structure, SAPO34, SAPO44, etc. having a CHA structure, SAPO17, etc. having an ERI structure or SAPO37, etc. having a FAU structure may be mentioned. Preferred is one having a CHA structure, and particularly preferred is SAPO34.

They may be various commercial products, or it is possible to use ones synthesized by a known method disclosed in e.g. "Verified Synthesis of Zeolitic Materials" (2<sup>nd</sup> Revised Edition 2001 Elsevier) published by the above IZA.

#### MODIFIED SOLID ACID CATALYST

Among solid acid catalysts in the present invention, the above mentioned crystalline porous silicate and the above mentioned crystalline porous aluminophosphate are preferably ones modified with metal elements of Groups 1 to 14 of the Periodic Table other than the silicon and aluminum elements.

The metal elements of Groups 1 to 14 of the Periodic Table other than the silicon and aluminum elements, to be used for modifying the crystalline porous silicate and the crystalline porous aluminophosphate in the present invention, are preferably metal elements of Groups 1 to 4 and Groups 7 to 13. Among the metal elements of Groups 1 to 4, metal elements of Groups 1 to 3 are preferred, and metal elements of Groups 1 and 2 are more preferred. Further, among the metal elements of Groups 7 to 13,

metal elements of Group 7 are preferred.

Further, among the metal elements of Groups 1 to 14 of the Periodic Table, with respect to Groups 1 and 2, metal elements in the third to fifth periods of the Periodic Table are preferred, metal elements in the fourth and fifth periods are more preferred, and metal elements in the fourth period are particularly preferred. Further, with respect to Groups 3 to 14, metal elements in the fourth and fifth periods in the Periodic Table are preferred, and metal elements in the fourth period are more preferred. Specific examples of such preferred metal elements may, for example, be Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Sc, Y, lanthanoid elements, Mn and Ni. Among them, metal elements to modify a crystalline porous silicate, metal elements of Groups 1 to 4, specifically, Na, K, Rb, Cs, Mg, Ca, Sr and Ba, are preferred, and Na, K, Mg, Ca, Sr and Ba are more preferred. Further, as metal elements to modify a crystalline porous aluminophosphate, metal elements in Groups 7 to 13, specifically Mn and Ni, are preferred, and Mn is more preferred.

Further, a zeolite of a structure represented by the above BEA, ERI, FAU, MFI, MOR, MWW or OFF by a code stipulated by the above IZA, is preferably one modified with a metal element of Group 2 of the Periodic Table.

#### MODIFYING METHOD

In the present invention, as a method for modifying

the above crystalline porous silicate or the above crystalline porous aluminophosphate with the above metal elements of Groups 1 to 14, it is possible to employ any one of (A) a method wherein the crystalline porous  
5 silicate or the crystalline porous aluminophosphate is produced in the presence of a compound having the above metal element of Groups 1 to 14 of the Periodic Table in the process for producing the crystalline porous silicate or the crystalline porous aluminophosphate, (B) a method  
10 wherein the crystalline porous silicate or the crystalline porous aluminophosphate is treated with a compound of the above metal element of Groups 1 to 14 of the Periodic Table, and a method of using (A) and (B) in combination.

15 As the compound of the above metal element of Groups 1 to 14 of the Periodic Table to be used for the modification, a salt, oxide or hydroxide of the metal of Groups 1 to 14 of the Periodic Table is, for example, employed. As the salt, an inorganic salt such as a  
20 nitrate, phosphate or chloride, or an organic salt such as a carboxylate such as an acetate, or a carbonate, may, for example, be employed.

Further, as a method for producing the crystalline porous silicate or the crystalline porous  
25 aluminophosphate in the presence of a compound of the above metal element of Groups 1 to 14 of the Periodic Table in the process for producing the crystalline porous

silicate or the crystalline porous aluminophosphate according to the above (A), specifically, in accordance with method disclosed, for example, in JP-A-59-97523 and JP-A-3-101628, the compound of the metal element of  
5 Groups 1 to 14 of the Periodic Table is permitted to be present in the raw material for the production of the crystalline porous silicate or the crystalline porous aluminophosphate to have the metal element introduced into the crystal lattice thereby to obtain a crystalline  
10 porous silicate modified with such a metal element, a so-called crystalline metal silicate such as metal silicate, metalloaluminosilicosilicate, metalloaluminophosphosilicate, metaborosilicate or metalloaluminoborosilicate, or a crystalline porous  
15 aluminophosphate similarly modified, a so-called crystalline metalloaluminophosphate such as metalloaluminophosphate, metasilicoaluminophosphate or metalloboroaluminophosphate.

Further, as the method for treating the above  
20 crystalline porous silicate or the above crystalline porous aluminophosphate with a compound of the above metal element of Groups 1 to 14 of the Periodic Table according to the above (B), specifically, the following method (B-1), (B-2) or (B-3) may, for example, be used.  
25 (B-1): The above crystalline porous silicate or the above crystalline porous aluminophosphate is subjected to ion exchange by means of a solution containing the

compound of the above metal element of Groups 1 to 14 of the Periodic Table in accordance with a usual method to introduce the metal element of Groups 1 to 14 of the Periodic Table into the crystal lattice thereby to obtain  
5 a crystalline porous silicate modified with such a metal element, i.e. the above mentioned crystalline metallosilicate, or a crystalline porous aluminophosphate likewise modified i.e. the above mentioned crystalline metalloaluminophosphate.

10 (B-2): The above crystalline porous silicate or the above crystalline porous aluminophosphate is surface-treated by e.g. a dipping method wherein it is dipped in a solution containing the compound of the above metal element of Groups 1 to 14 of the Periodic Table in  
15 accordance with a usual method, followed by filtration and separation by e.g. centrifugal separation, or by an impregnation method wherein it is immersed in a solution containing the compound of the above metal element, followed by evaporation of the solvent to dryness,  
20 thereby to obtain a crystalline porous silicate or crystalline porous aluminophosphate, modified with the metal element of Groups 1 to 14 of the Periodic Table.

In such a case, the solvent for the solution containing the compound of the above metal element is not  
25 particularly limited, but usually, water or an alcohol is employed, and water is preferred. Further, the concentration of the solution is usually at least 0.01

wt% and at most the saturated concentration. In the dipping method, it is necessary to consider the water absorption of the crystalline porous silicate or the crystalline porous aluminophosphate, but it is preferred  
5 to employ a solution having a high concentration, whereby the metal element can be efficiently introduced.

Further, the treatment is carried out so that the amount of the compound of the metal element of Groups 1 to 14 of the Periodic Table in the modified crystalline porous  
10 silicate or crystalline porous aluminophosphate will be usually at least 0.001, preferably at least 0.01, more preferably at least 0.1 and usually at most 1,000, preferably at most 100, more preferably at most 10, by weight ratio of the metal compound to the silicate or  
15 aluminophosphate.

(B-3): The above crystalline porous silicate or the above crystalline porous aluminophosphate is physically mixed with the compound of the above metal element of Groups 1 to 14 of the Periodic Table in accordance with a  
20 usual method, whereby it is possible to obtain a crystalline porous silicate or crystalline porous aluminophosphate, modified with the metal element of Groups 1 to 14 of the Periodic Table.

In such physical mixing, an oxide or a carbonate is  
25 preferred from the viewpoint of the stability under the mixing condition of the compound of the metal element of Groups 1 to 14 of the Periodic Table. Further, the above

crystalline porous silicate or the above crystalline porous aluminophosphate, and the compound of the metal element of Groups 1 to 14 of the Periodic Table, are in the form of particles having a particle size of usually at least 0.01 mm and at most 5 mm. However, for the mixing treatment to be carried out efficiently, the smaller the particle size of the compound of the metal element, the better. The mixing ratio of the crystalline porous silicate or crystalline porous aluminophosphate to the compound of the metal element of Groups 1 to 14 of the Periodic Table is usually at least 0.001, preferably at least 0.01, more preferably at least 0.1 and usually at most 100, preferably at most 10, more preferably at most 5, by weight ratio as the metal atoms of the metal element to the crystalline porous silicate or aluminophosphate. Further, the mixing apparatus at that time is not particularly limited, and mixing can be carried out by means of a usual stirring apparatus. However, from the viewpoint of efficiency, it is preferred to employ an apparatus whereby pulverization and mixing can be simultaneously carried out. The mixing time may change depending upon the amount to be treated, but is usually at least 1 second, preferably at least 1 minute and usually at most 10 hours, preferably at most 1 hour, more preferably at most 30 minutes.

Among the above modifying methods, one obtainable by the method (A) tends to be a solid acid catalyst having a

high initial performance, specifically a high propylene selectivity, as a catalyst, and one obtainable by the method (B) tends to be a solid acid catalyst excellent in each of the selectivity and the catalytic life.

5 (ii) LAMELLAR ZEOLITE

The lamellar zeolite in the present invention is a zeolite in a state where a layer of a lamellar precursor is peeled, as disclosed, for example, in "Science and Engineering of Zeolite" p. 10 (published by Kodansha  
10 Ltd., 2000). The lamellar zeolite is aluminosilicate having an acid strength equal to zeolite. It has a structural regularity having short periodicity and no long periodicity.

The lamellar zeolite is usually aluminosilicate,  
15 wherein the Si/Al molar ratio is at least 5, preferably at least 7.5, more preferably at least 10 and at most 10,000, preferably at most 5,000, further preferably at most 1,000. It may be one having a part or all of Al substituted by an atom from 2 to 14 in the Periodic  
20 Table. The atom for substitution may preferably be B, Ti, V, Fe, Zn, Ga, Ge, Zr or Sn.

The lamellar zeolite has a BET specific surface area of usually at least 300 m<sup>2</sup>/g, preferably at least 400 m<sup>2</sup>/g, more preferably at least 500 m<sup>2</sup>/g and usually at  
25 most 2,000 m<sup>2</sup>/g, preferably at most 1,800 m<sup>2</sup>/g, more preferably at most 1,500 m<sup>2</sup>/g. Further, the proportion of the specific surface area of pores of from 1.7 nm to

30 nm in the entire BET specific surface area is usually at least 0.4, preferably at least 0.5, more preferably at least 0.6. In XRD, when measured by Cu K $\alpha$  lines, it shows no maximum peak at a spacing  $d$  of lattice planes  
5 being at least 17 Å and shows a peak at from 3 to 4.5 Å.

The pore volume is usually at least 0.3 cc/g, preferably at least 0.5 cc/g and usually at most 3 cc/g, preferably at most 2 cc/g.

As a specific example of the lamellar zeolite, ITQ-  
10 2, YNU-1 or ITQ-6 may, for example, be mentioned, and ITQ-2 is preferred.

#### METHOD FOR PRODUCING LAMELLAR ZEOLITE

As a common method for preparing a lamellar zeolite, one prepared by a known method disclosed, for example, in  
15 Journal of Catalysis 186, 57-63, (1999) or in J. Am. Chem. Soc. 122, 2804-2809, (2000) may be employed. The method will be described in detail, but it should be understood that the method for producing a lamellar zeolite to be used as the catalyst of the present  
20 invention is by no means restricted thereto.

Firstly, a silica source, an alumina source, water and a template, and, if necessary, a mineralizer, are mixed, and the mixture is subjected to hydrothermal synthesis. As the silica source, water glass, silica  
25 sol, fine powder silica or an alkyl silicate such as ethyl silicate may be used. As the aluminum source, an inorganic salt such as a nitrate, sulfate or chloride of

aluminum, an organic salt such as an acetate, a hydroxide, an oxide, a pseudoboehmite, an alkoxide or sodium aluminate may, for example, be used. As the template, a quaternary alkylammonium salt, an alkylamine, a diamine, an alcoholamine, an alcohol, an ether, an amide, an alkyl urea or a cyanoalkane may, for example, be used, and a quaternary alkylammonium salt or an amine is preferred.

As the mineralizer, a hydroxide, a hydrogen carbonate or carbonate of an alkali metal or an alkaline earth metal may, for example, be used.

With respect to the ratio of the silica source to the aluminum source,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  is usually at least 1, preferably at least 5, more preferably at least 10 and usually at most 1,000, preferably at most 500, more preferably at most 300.

The molar ratio of water to the silica source is such that  $\text{H}_2\text{O}/\text{SiO}_2$  is usually at least 1, preferably at least 2, more preferably at least 3 and usually at most 200, preferably at most 150, more preferably at most 120.

The ratio of the mineralizer to the silica source is such that the molar ratio of the metal atoms of the mineralizer to  $\text{SiO}_2$  is usually at least 0.0001, preferably at least 0.001, more preferably at least 0.01 and usually at most 20, preferably at most 10, more preferably at most 8.

The ratio of the template to the silica source is

such that the molar ratio of the template to  $\text{SiO}_2$  is usually at least 0.01, preferably at least 0.02, more preferably at least 0.05 and usually at most 20, preferably at most 10, more preferably at most 6.

5       The aqueous mixture thus prepared is heated to a temperature of usually at least  $80^\circ\text{C}$ , preferably at least  $90^\circ\text{C}$  and usually at most  $260^\circ\text{C}$ , preferably at most  $220^\circ\text{C}$  and subjected to hydrothermal synthesis with or without stirring under natural pressure or a higher pressure.

10       The time required for the hydrothermal synthesis is usually at least one hour, preferably at least 5 hours and usually at most 30 days.

      The lamellar precursor thus formed is obtained by separating it by e.g. filtration after the hydrothermal  
15   synthesis.

      For a high silica zeolite, an organic substance commonly called a template is used during the hydrothermal synthesis, firstly a precursor as made containing the template is synthesized, and the precursor  
20   is fired, whereby interlayer dehydration condensation takes place to form a zeolite. In such a zeolite, one obtainable by the hydrothermal synthesis may be one which is a lamellar precursor. As an index to determine whether or not the product is a lamellar precursor, the  
25   state as made is different from the structure after removal of the template by calcination. This is evident, for example, by the XRD analysis.

The lamellar precursor may, for example, be a precursor for a MWW zeolite which becomes e.g. MCM22, SSZ25, ITQ1, ERB1 or PSH3 by calcination, a precursor so-called PREFER which becomes FER by calcination, or a  
5 lamellar silicate such as PLS-1, RUB-15 or RUB-18.

In a case where a lamellar zeolite is obtained from the lamellar precursor, usually, the interlayer of such a lamellar precursor is broadened by means of e.g. a surfactant, followed by removal of an organic substance  
10 thereby to peel a layer to obtain a lamellar zeolite.

To broaden the interlayer, the lamellar precursor is treated with an aqueous solution containing a surfactant and a quaternary ammonium salt. As the surfactant, a water-soluble long chain organic compound is usually  
15 employed, and a hydroxide or halide of octyltrimethyl ammonium, dodecyltrimethyl ammonium or cetyltrimethyl ammonium, and as the halide, a chloride or a bromide is preferred.

As the quaternary ammonium salt, it is possible to  
20 employ an alkyl ammonium having an alkyl group of at most 8 carbon atoms, such as tetrapropyl ammonium.

The blend ratio of the quaternary ammonium salt to the surfactant is such that the quaternary ammonium salt/surfactant is usually at least 0.1, preferably at  
25 least 0.2, more preferably at least 0.3 and usually at most 10, preferably at most 5, more preferably at most 3.

The concentration of the aqueous solution is such

that the sum of the number of moles of the surfactant and the number of moles of the quaternary ammonium salt, is usually at least 0.1 mol/l, preferably at least 0.2 mol/l, more preferably at least 0.3 mol/l and usually at most 10 mol/l, preferably at most 5 mol/l, more preferably at most 3 mol/l.

The amount of the aqueous solution is such that the weight proportion of the lamellar precursor to the aqueous solution is usually at least 2, preferably at least 4, more preferably at least 10 and usually at most 200, preferably at most 100, more preferably at most 50.

The treating temperature is usually at least 20°C, preferably at least 40°C, more preferably at least 80°C and usually at most 120°C, preferably at most 110°C, more preferably at most 100°C. The treating time is usually at least 1 hour, preferably at least 7 hours and usually at most 40 hours, preferably at most 25 hours.

After the treatment, the product is, as it is or after once subjected to filtration and washing with water, formed again into a slurry with water, and then layer peeling is carried out. The layer peeling is usually carried out by a known peeling method such as intensive stirring, ultrasonic treatment or spray drying. In the case of intensive stirring or ultrasonic treatment, the peeling time is usually at least 0.5 hour, preferably at least 1 hour and usually at most 100 hours, preferably at most 20 hours.

After the layer peeling, the lamellar zeolite will be separated. The separation may be carried out by filtration or by centrifugal separation. However, in a case where the size of the lamellar zeolite is small, an acid such as hydrochloric acid or sulfuric acid may usually be added for flocculation in order to increase the recovery efficiency.

Thus, a lamellar zeolite containing a template will be obtained. However, in order to remove the template, drying and calcination are carried out to obtain a lamellar zeolite.

The drying temperature is usually at least 80°C and at most 150°C, and the drying is carried out for usually at least 10 minutes, preferably at least 30 minutes and usually at most 24 hours, preferably at most 12 hours. The calcinating temperature is usually at least 300°C, preferably at least 400°C and usually at most 800°C, preferably at most 600°C, and the calcination is carried out for usually at least 10 minutes, preferably at least 30 minutes and usually at most 24 hours, preferably at most 12 hours.

As the lamellar zeolite synthesized as described above, ITQ-2 from a MWW type zeolite precursor or ITQ-6 from YNU-1 or PREFER, may, for example, be mentioned.

The lamellar zeolite thus produced has a short periodical structural regularity and thus has active sites such as acid sites like usual zeolite and yet is

layered than usual zeolite, whereby the outer surface is large. By virtue of such characteristics, in the present invention, it is advantageous for e.g. dispersion and becomes a catalyst excellent in selectivity and  
5 durability.

The above catalyst may be used for the reaction as it is, or may be granulated or molded by means of a binder or substance inert to the reaction and then used for the reaction. As the binder or substance inert to  
10 the reaction, alumina or alumina sol, silica, silica gel, quartz, or a mixture thereof may, for example, be mentioned. Mixing with such a substance is effective for reduction of the cost of the entire catalyst or for a function as a heat sink for assisting heat insulation at  
15 the time of regeneration of the catalyst, and it is also effective for high densification of the catalyst and for increasing the catalyst strength.

### (3) REACTION CONDITIONS IN THE PRESENT INVENTION

The reaction mode in the process of the present  
20 invention is not particularly limited so long as the feed materials constitute a gas phase in the reaction zone, and a known gas phase reaction process using a fluidized bed reactor, a movable bed reactor or a fixed bed reactor, may be employed. Further, the reaction may be  
25 carried out in any form of a batch system, a semicontinuous system or a continuous system, but it is preferred to carry it out by a continuous system. Such a

method may be a method employing a single reactor or a method employing a plurality of reactors disposed in series or in parallel.

According to the present invention, in a process for  
5 producing propylene which comprises bringing ethylene in contact with methanol and/or dimethyl ether, the reaction conditions are adjusted so that the amount of ethylene in a reaction mixture being discharged from the reaction system is reduced as compared with the amount of ethylene  
10 being fed to the reaction system, and propylene is obtained in a yield of at least 40 mol% based on the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system.

15 As reaction conditions to be adjusted for this purpose, the pressure and the raw material composition, and further, in a case where the reaction is carried out in a continuous system, the rate for feeding the raw materials, are particularly important.

20 The reaction pressure is usually less than 2 MPa. The reaction pressure is preferably at most 1 MPa, more preferably at most 0.7 MPa, inclusive of a natural pressure. Further, the lower limit is not particularly limited, but is usually at least 0.1 kPa, preferably at  
25 least 7 kPa, more preferably at least 50 kPa.

To accomplish the above objects, the reaction pressure is adjusted within a range of at least 0.1 kPa

and less than 2 MPa. In such a case, when the reaction pressure is increased, ethylene as the reaction raw material or propylene as the desired product is likely to polymerize with an olefin present in the reaction system, whereby the yield of propylene tends to decrease, and when the reaction pressure is lowered, the reaction rate tends to be slow. Accordingly, the pressure is adjusted taking into such tendencies into consideration.

With respect to the raw material composition, the amount of ethylene being fed to the reaction system is an excessive amount to the methanol and dimethyl ether being fed to the reaction system, i.e. the amount of ethylene being fed to the reaction system is usually at least 1, preferably at least 1.8, more preferably at least 3, by molar ratio to the sum of the number of moles of methanol and two times the number of moles of dimethyl ether. On the other hand, if ethylene is too excessive, there will be a problem with respect to the cost, the amount of by-products to be formed and cumbersomeness in operation, etc. Accordingly, as the upper limit, the amount of ethylene being fed to the reaction system is usually at most 20, more preferably at most 10, particularly preferably at most 6 by molar ratio to the sum of the number of moles of methanol and two times the number of moles of dimethyl ether.

To accomplish the above objects, the amount of ethylene being fed to the reaction system is adjusted

within a range of at least 1 and at most 20 by molar ratio to the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system. In such a case, when  
5 the amount of ethylene is increased, a reaction of ethylene itself is likely to take place, whereby the amount of by-products tends to increase, and when the amount of ethylene is lowered, a reaction of methanol and/or dimethyl ether itself is likely to take place,  
10 whereby ethylene, etc. tend to form. Accordingly, the amount is adjusted taking such tendencies into consideration.

Further, adjusting the amount of ethylene being fed to the reaction system within a range of at least 1 and  
15 at most 20 by molar ratio to the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system, does not mean adjustment of only the amount of ethylene. One or both of the amount of ethylene and the  
20 amount of methanol and/or dimethyl ether may be adjusted so that consequently, the amount of ethylene being fed to the reaction system is adjusted within a range of at least 1 and at most 20 by molar ratio to the sum of the number of moles of methanol and two times the number of  
25 moles of dimethyl ether.

As the raw material feeding rate to carry out the reaction in a continuous system, the weight hourly space

velocity (WHSV) per the weight of a catalytically active component, of the sum of methanol and dimethyl ether calculated as methanol, which are being fed to the reaction system, is usually at most about  $70 \text{ hr}^{-1}$ , preferably at most  $50 \text{ hr}^{-1}$ , more preferably at most about  $30 \text{ hr}^{-1}$ , further preferably at most  $20 \text{ hr}^{-1}$ . Here, if WHSV is too small, the yield of the desired product is likely to decrease due to an increase of by-products, and separation tends to be cumbersome. Accordingly, it is usually at least about  $0.01 \text{ hr}^{-1}$ , preferably at least  $0.05 \text{ hr}^{-1}$ , more preferably at least  $0.1 \text{ hr}^{-1}$ , further preferably at least  $0.5 \text{ hr}^{-1}$ .

To accomplish the above objects, the weight hourly space velocity (WHSV) per the weight of a catalytically active component, of the sum of methanol and dimethyl ether calculated as methanol, which are being fed to the reaction system, is adjusted within a range of at least  $0.01 \text{ hr}^{-1}$  and at most  $70 \text{ hr}^{-1}$ . If WHSV is small, a consecutive reaction is likely to take place as mentioned above, whereby by-products tend to increase, and the formed propylene tends to be consumed. Accordingly, it is adjusted taking such tendencies into consideration.

In a case where the reaction is carried out in a batch system or in a semicontinuous system, the reaction time may suitably be set depending upon the desired yield of propylene.

Here, if unreacted methanol and unreacted dimethyl

ether are present in a large amount in the discharged component from the reaction system, the utilization ratio of methanol and dimethyl ether decreases, and no cost merits will be obtained. Not only that, the load in  
5 separation from propylene as the desired product and in the process for purification of propylene will be large, such being undesirable. Further, this reaction is an exothermic reaction, and if a large amount of methanol will react all at once, the temperature control tends to  
10 be difficult due to the heat of reaction generated, and further influence such as a decrease in the yield of the desired product or shortening of the catalyst life, may result. Accordingly, methanol and dimethyl ether are fed preferably in a divided fashion.

15       The method for feeding in a divided fashion varies depending upon the design of the reaction system as to e.g. whether or not a single reactor is employed or whether a plurality of reactors are disposed in series or in parallel. For example, there may be a method wherein  
20 in a single reactor, a plurality of methanol and dimethyl ether inlets are provided to carry out feeding in a divided fashion, or a method wherein in each of a plurality of reactors, methanol and dimethyl ether inlets are provided to carry out feeding in a divided fashion.  
25 Here, feeding in a divided fashion is preferably carried out in such a manner that upon consumption of at least 90% of the methanol and dimethyl ether previously fed,

the additional methanol and dimethyl ether will be fed.

The reaction conditions such as the reaction temperature in the process of the present invention may optionally be set in accordance with a known process. If  
5 unreacted methanol and unreacted dimethyl ether are present in a large amount in the discharged component from the reaction system, the utilization ratio of methanol and dimethyl ether will decrease, and no cost merit will be obtainable. Not only that, the load in  
10 separation from propylene as the desired product and in the purification process of propylene will increase, such being undesirable. Accordingly, as the above various reaction conditions, it is preferred to employ conditions whereby the raw material methanol and dimethyl ether will  
15 be completely converted.

Here, the reaction temperature may depend on the type of the catalyst to be used, but is usually at least about 200°C, preferably at least about 250°C, more preferably at least about 300°C, and the upper limit is  
20 usually at most about 700°C, preferably at most about 600°C, more preferably at most about 500°C. If the reaction temperature is too low, the reaction rate tends to be small, the rate for formation of the desired product tends to be remarkably slow, and unreacted raw  
25 materials tend to remain in a large amount. On the other hand, if the reaction temperature is too high, the yield of the desired product tends to be low.

Further, as the reaction continues, the catalyst is likely to undergo coking in the reactor, whereby the reaction activities will decrease. In such a case, the catalyst may be withdrawn from the reactor, and all or a  
5 part of the coke is removed, for example, by oxidizing the accumulated coke in an oxygen-containing atmosphere, thereby to regenerate the catalyst. Such a regenerated catalyst may be reintroduced into the reactor. From the viewpoint of such withdrawal and reintroduction of the  
10 catalyst, it is preferred to employ a process using a movable bed reactor or a fluidized bed reactor rather than a fixed bed, since the operation is thereby simple.

In the process of the present invention, water will be formed as a by-product in the reaction system as the  
15 reaction proceeds. However, it is preferred to supply water to the reaction system by a method such as adding water to the reaction raw material to let water (i.e. steam) be coexistent in the reaction system from the initial stage of the reaction. By letting water be  
20 present in the system, there will be a function to suppress formation of coke which causes deactivation of the catalyst, and it is possible to obtain an effect to prolong the catalyst life and to suppress formation of paraffins or oligomerization of the formed olefin thereby  
25 to increase the selectivity of the desired propylene.

The amount of water to be supplied to the reaction system may depend on the type of the solid acid catalyst to be

used or other reaction conditions, but is usually at least 0.025, preferably at least 0.1, more preferably at least 0.5, by molar ratio to the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being supplied to the reaction system. If water is too much, the reaction rate will decrease, and there will be a problem such that the yield of the desired product will decrease or the catalyst itself will react with water and undergoes modification. Accordingly, it is usually at most 15, preferably at most 10, more preferably at most 5, by such molar ratio.

The reaction product mixture obtainable by the above reaction is one containing propylene as the main component and ethylene as unreacted raw material, and olefins having at least 4 carbon atoms are also contained. The amount of by-products such as the above paraffins, olefins and aromatic hydrocarbons is such that the molar concentration in the hydrocarbon component at the outlet of the reactor is at most 30%, preferably at most 15%. Further, it contains ethylene in an amount smaller than the amount of ethylene being fed to the reaction system and contains propylene in an amount of at least 40 mol%, preferably at least 50 mol%, based on the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system.

#### (4) METHOD FOR SEPARATING THE PRODUCT

In a case where the desired propylene is to be isolated from the above reaction product mixture, the mixture may be introduced to a known separation/purification facility as in an ethylene  
5 cracker process, whereby depending upon the respective components, recovery, purification, recycling or discharge treatment may be applied.

In the present invention, the reaction product by the reaction of ethylene with methanol and/or dimethyl  
10 ether contains olefins having at least 4 carbon atoms formed as by-products in addition to the formed propylene and unreacted ethylene, methanol and dimethyl ether, and further contains a carrier such as ethane, etc. For purification of propylene, a methane-removing column, an  
15 ethane-removing column, a propane-removing column, etc. should basically be provided as propylene production facilities. However, by recycling the reaction product to the above mentioned facility for the production of olefins by thermal decomposition of naphtha, to the  
20 facility for the production of lower olefins from methanol and/or dimethyl ether, or to the separation/purification system in the facility for the production of ethylene by steam cracking of ethane, a part of equipments which should basically be provided for  
25 the propylene production facilities may be omitted, and the facilities can be minimized.

For example, in a case where propylene is produced

by reacting ethylene obtained by the facility for the production of olefins by thermal decomposition of naphtha, with a gas containing methanol and/or dimethyl ether, it is preferred to introduce the reaction product  
5 to the methane-removing column and/or the ethane-removing column and/or the propane-removing column in the facility for the production of olefins. It is thereby possible to substantially change the yield balance of ethylene and propylene to increase the propylene/ethylene amount ratio  
10 in the production of olefins by thermal decomposition of naphtha, and it is also possible to improve the efficiency in the operation of the facility for the production of olefins by the thermal decomposition of naphtha and at the same time to minimize the facility for  
15 the production of propylene from ethylene.

The reaction product contains olefins having at least four carbon atoms formed as by-products in addition to the formed propylene and unreacted ethylene, and further, in a case where the top fraction in the above  
20 front end methane-removing process and the above mentioned front end propane-removing process is used as the ethylene raw material, ethane will also be contained, or in a case where the top fraction in the above front end ethane-removing process is used as the ethylene raw  
25 material, ethane, methane and hydrogen may, for example, be contained. Accordingly, in the purification of propylene, the propylene production facilities for the

process of the present invention are preferably provided with the methane-removing column, the ethane-removing column, the propane-removing column, etc., but depending upon the operation state in the facility for the

5 production of olefins, at least a part of the reaction product may be introduced to the methane-removing column and/or the ethane-removing column and/or the propane-removing column in that facility, whereby it is possible to improve the efficiency in the operation of the

10 facility for the production of olefins by thermal decomposition of naphtha and at the same time to minimize the number of equipments to be provided for the facility for the production of propylene and/or to minimize the capacity of the equipment installed.

15 In a case where a methane-removing column and/or an ethane-removing column and/or a propane-removing column are installed in the facility for the production of propylene, depending upon the operation states of the facility for the production of olefins and the facility

20 for the production of propylene, it will be possible to introduce the product from the facility for the production of olefins to the methane-removing column and/or the ethane-removing column and/or the propane-removing column of the facility for the production of

25 propylene, whereby the allowable range of the facility for the production of olefins can be broadened, and the operation conditions can be optionally changed to

maximize the efficiency of the overall process including the facility for the production of olefins and the facility for the production of propylene.

In a case where as the ethylene, ethylene obtained  
5 by the facility for the production of lower olefins is employed, it is preferred to recycle the obtained reaction product composed mainly of propylene to a separation/purification system of the facility for the production of lower olefins.

10 In such a case, the separation/purification system of the facility for the production of lower olefins to which the reaction product is to be recycled, may, for example, be a cleaning column or a piping thereto, or the ethylene/ethane-removing column or a piping thereto, in  
15 the facility.

Here, the ethylene-containing fraction is preferably recycled as the raw material for the reaction.

Further, in the above reaction, water is also formed as a by-product. Accordingly, it is also preferred that  
20 a part of water formed in the reaction system is added to the raw material and recycled in the reaction system.

#### EXAMPLES

Specific embodiments of the present invention will  
25 be shown in the following Examples. However, it should be understood that the present invention is by no means restricted to such Examples.

## EXAMPLE 1-1

For the reaction, an atmospheric pressure fixed bed flow reaction apparatus was used, and a mixture comprising 0.1 g of a catalyst and 0.5 g of a diluent quartz sand was packed in a reaction tube made of PYREX (registered trademark) and having an outer diameter of 6 mm. As the catalyst, SAPO34 prepared in accordance with US Patent 4,440,871 was used, and the reaction was carried out under the following reaction conditions. In Table 1, the reaction results are shown, and gas chromatography was used for the analysis of the product. The methanol conversion, the hydrocarbon composition and the propylene yield represent the values upon expiration of 70 minutes after setting the reaction conditions.

## 15 REACTION CONDITIONS

Reaction temperature: 400°C

Methanol: 6.5 mol%

Ethylene/methanol (molar ratio) = 5

Water/methanol (molar ratio) = 4

20 Methanol WHSV = 0.5 hr<sup>-1</sup>

## EXAMPLE 1-2

The reaction was carried out in the same manner as in Example 1-1 except that as the catalyst, ZSM5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 300) prepared in accordance with the method disclosed in the journal of Institute of Petroleum, 24, (5), 275-280 (1981), was used.

## COMPARATIVE EXAMPLE 1

The reaction was carried out in the same manner as in Example 1-1 except that as the catalyst, SAPO-34 was used, and ethylene/methanol (molar ratio) was changed to 0.5.

5 TABLE 1

|                                                                                | Ex. 1-1 | Ex. 1-2 | Comp.<br>Ex. |
|--------------------------------------------------------------------------------|---------|---------|--------------|
| Catalyst                                                                       | SAPO-34 | ZSM-5   | SAPO-34      |
| ETY/MeOH (molar ratio)                                                         | 5       | 5       | 0.5          |
| H <sub>2</sub> O/MeOH (molar ratio)                                            | 4       | 4       | 4            |
| MeOH conversion (%)                                                            | 100     | 100     | 100          |
| Hydrocarbon composition in<br>the discharged component<br>from the reactor (%) |         |         |              |
| Ethylene                                                                       | 61.1    | 60.1    | 73.3         |
| Propylene                                                                      | 28.2    | 14.2    | 18.2         |
| Butene                                                                         | 3.0     | 10.8    | 5.1          |
| Propylene yield (mol%) based<br>on MeOH fed                                    | 120.4   | 56.6    | 15.7         |
| (ETY=ethylene, MeOH=methanol)                                                  |         |         |              |

## EXAMPLES 2 TO 14

### PREPARATION OF SOLID ACID CATALYST

#### 10 PREPARATION EXAMPLE 1

Crystalline porous aluminosilicate H-type ZSM5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 300) having a MFI structure was obtained in accordance with the method disclosed in journal of Institute of Petroleum, 24, (5), 275-280 (1981). The  
 15 composition of this crystalline porous aluminosilicate was analyzed by an X-ray fluorescence analysis, and the results are shown in Table 2.

#### PREPARATION EXAMPLE 2

1 g of the crystalline porous aluminosilicate obtained in Preparation Example 1 was mixed with 0.36 g of calcium carbonate obtained by calcinating calcium acetate at 500°C for 10 hours and then at 550°C for 6  
5 hours, in a mortar in a solid state, to obtain a calcium-mixed crystalline porous aluminosilicate.

#### PREPARATION EXAMPLE 3

1 g of the crystalline porous aluminosilicate obtained in Preparation Example 1 was mixed with 0.36 of  
10 strontium carbonate obtained by calcinating strontium acetate at 500°C for 18 hours, in a mortar in a solid state, to obtain a strontium-mixed crystalline porous aluminosilicate.

#### PREPARATION EXAMPLE 4

15 Crystalline porous aluminosilicate H-type ZSM5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$ ) having a MFI structure was obtained in accordance with the method disclosed in journal of Institute of Petroleum, 24, (5), 275-280 (1981). 2 g of this crystalline porous aluminosilicate was mixed with an  
20 aqueous solution having 1.23 g of calcium acetate monohydrate dissolved in 20 ml of water, and the mixture was stirred at about 80°C for about 20 hours and then evaporated to dryness at from 100 to 120°C, followed by calcination at 200°C for two hours and then at 500°C for  
25 18 hours in air, to obtain a calcium-supported crystalline porous aluminosilicate. The composition of this aluminosilicate was analyzed by X-ray fluorescence,

and the results are shown in Table 2.

#### PREPARATION EXAMPLE 5

Crystalline porous aluminoborosilicate as a zeolite having a MFI structure was obtained in accordance with the method disclosed in journal of Institute of Petroleum, 24, (5), 275-280 (1981) by using boric acid further as a raw material. The composition of this crystalline porous aluminoborosilicate was analyzed by a chemical analysis and X-ray fluorescence analysis, and the results are shown in Table 2. 1 g of this crystalline porous aluminoborosilicate was mixed with an aqueous solution having 0.4 g of calcium acetate monohydrate dissolved in 10 ml of water, and the mixture was stirred at about 80°C for about 20 hours and then evaporated to dryness at from 100 to 120°C, followed by calcination at 200°C for two hours and then at 500°C for 18 hours in air, to obtain a calcium-supported crystalline porous aluminoborosilicate.

#### PREPARATION EXAMPLE 6

To an aqueous solution having 0.38 g of aluminum nitrate nonahydrate and 0.45 g of calcium acetate monohydrate dissolved in 30 g of water, 20 g of colloidal silica containing 30 wt% of silica (manufactured by Catalysts & Chemicals Industries Co., Ltd.) and 14 g of water were added with stirring, and an aqueous solution having 0.42 g of sodium hydroxide dissolved in 6.67 g of water, was added thereto. Further, an aqueous solution

having 2.7 g of tetra-n-butylammonium bromide dissolved in 10 g of water, was added, and the mixture was vigorously stirred for two hours. The charged molar ratio at that time was such that  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ , and  
5  $\text{CaO}/\text{SiO}_2 = 0.025$ . This gel mixture was charged into an autoclave having an internal capacity of 100 ml and subjected to hydrothermal treatment at  $180^\circ\text{C}$  for 48 hours under natural pressure. The product was collected by filtration, washed with water, dried at  $120^\circ\text{C}$  overnight  
10 and calcinated at  $550^\circ\text{C}$  for 6 hours in air. 1 g of the product was mixed with 15 ml of 0.8 N hydrochloric acid, subjected to stirring treatment at room temperature for 24 hours, then thoroughly washed with water, then dried at  $120^\circ\text{C}$  overnight and calcinated at  $550^\circ\text{C}$  for 6 hours in  
15 air, to obtain a H-type calcium-containing crystalline porous aluminosilicate. The composition of this calcium-containing crystalline porous aluminosilicate was analyzed by X-ray fluorescence, and the results are shown in Table 2. This calcium-containing crystalline porous  
20 aluminosilicate was mixed with 0.36 g of calcium carbonate obtained by calcinating calcium acetate at  $500^\circ\text{C}$  for 10 hours and then at  $550^\circ\text{C}$  for 6 hours, in a mortar in a solid state, to obtain a calcium-mixed H-type calcium-containing crystalline porous aluminosilicate.

#### 25 PREPARATION EXAMPLE 7

1 g of the calcium-containing crystalline porous aluminosilicate obtained in Preparation Example 6 was

mixed with 0.36 g of strontium carbonate obtained by calcinating strontium acetate at 500°C for 18 hours, in a mortar in a solid state, to obtain a strontium-mixed H-type calcium-containing crystalline porous  
5 aluminosilicate.

#### PREPARATION EXAMPLE 8

To an aqueous solution having 0.38 g of aluminum nitrate nonahydrate and 0.45 g of magnesium acetate tetrahydrate dissolved in 30 g of water, 20 g of  
10 colloidal silica containing 30 wt% of silica (manufactured by Catalysts & Chemicals Industries Co., Ltd.) and 14 g of water were added with stirring, and an aqueous solution having 0.42 g of sodium hydroxide dissolved in 6.67 g of water, was added thereto.  
15 Further, an aqueous solution having 2.7 g of tetra-n-butylammonium bromide dissolved in 10 g of water, was added, and the mixture was vigorously stirred for two hours. The charged molar ratio at that time was such that  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ , and  $\text{CaO}/\text{SiO}_2 = 0.025$ . This gel  
20 mixture was charged into an autoclave having an internal capacity of 100 ml and subjected to hydrothermal treatment at 180°C for 48 hours under natural pressure. The product was collected by filtration, washed with water, dried at 120°C overnight and calcinated at 550°C  
25 for 6 hours in air. 1 g of the product was mixed with 15 ml of 0.8 N hydrochloric acid, subjected to stirring treatment at room temperature for 24 hours and then

thoroughly washed with water, then dried at 120°C overnight and calcinated at 550°C for 6 hours in air, to obtain a H-type magnesium-containing crystalline porous aluminosilicate. The composition of this magnesium-  
5 containing crystalline porous aluminosilicate was analyzed by X-ray fluorescence, and the results are shown in Table 2.

#### PREPARATION EXAMPLE 9

1 g of the magnesium-containing crystalline porous  
10 aluminosilicate obtained in Preparation Example 8 was mixed with 0.36 g of calcium carbonate obtained by calcinating calcium acetate at 500°C for 10 hours and then at 550°C for 6 hours, in a mortar in a solid state, to obtain a calcium-mixed H-type magnesium-containing  
15 crystalline porous aluminosilicate.

#### PREPARATION EXAMPLE 10

1 g of the magnesium-containing crystalline porous aluminosilicate obtained in Preparation Example 8 was mixed with 0.36 g of magnesium oxide obtained by  
20 calcinating magnesium acetate at 500°C for 18 hours, in a mortar in a solid state, to obtain a magnesium-mixed H-type magnesium-containing crystalline porous aluminosilicate.

#### PREPARATION EXAMPLE 11

25 1 g of the magnesium-containing crystalline porous aluminosilicate obtained in Preparation Example 8 was mixed with 0.36 g of manganese oxide ( $\text{Mn}_2\text{O}_3$ ) obtained by

calcinating manganese oxalate at 500°C for 18 hours, in a mortar in a solid state, to obtain a manganese-mixed H-type magnesium-containing crystalline porous aluminosilicate.

5 PREPARATION EXAMPLE 12

To an aqueous solution having 0.38 g of aluminum nitrate nonahydrate and 0.65 g of barium acetate monohydrate dissolved in 30 g of water, 20 g of colloidal silica containing 30 wt% of silica (manufactured by  
10 Catalysts & Chemicals Industries Co., Ltd.) and 14 g of water were added with stirring, and an aqueous solution having 0.42 g of sodium hydroxide dissolved in 6.67 g of water, was added thereto. Further, an aqueous solution having 2.7 g of tetra-n-butylammonium bromide dissolved  
15 in 10 g of water, was added, and the mixture was vigorously stirred for two hours. The charged molar ratio at that time was such that  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ , and  $\text{BaO}/\text{SiO}_2 = 0.025$ . This gel mixture was charged into an autoclave having an internal capacity of 100 ml and  
20 subjected to hydrothermal treatment at 180°C for 48 hours under natural pressure. The product was collected by filtration, washed with water, dried at 120°C overnight and calcinated at 550°C for 6 hours in air. 1 g of the product was mixed with 15 ml of 0.8 N hydrochloric acid,  
25 subjected to stirring treatment at room temperature for 24 hours, then thoroughly washed with water, dried at 120°C overnight and calcinated at 550°C for 6 hours in

air, to obtain a H-type barium-containing crystalline porous aluminosilicate. The composition of this barium-containing crystalline porous aluminosilicate was analyzed by X-ray fluorescence, and the results are shown in Table 2. 1 g of this barium-containing crystalline porous aluminosilicate was mixed with 0.36 g of calcium carbonate obtained by calcinating calcium-acetate at 500°C for 10 hours and then at 550°C for 6 hours, in a mortar in a solid state, to obtain a calcium-mixed H-type barium-containing crystalline porous aluminosilicate.

#### PREPARATION EXAMPLE 13

To an aqueous solution having 0.09 g of aluminum phosphate and 0.34 g of calcium acetate monohydrate dissolved in 25 g of water, 15 g of colloidal silica containing 30 wt% of silica (manufactured by Catalysts & Chemicals Industries Co., Ltd.) was added with stirring, and an aqueous solution having 0.4 g of sodium hydroxide dissolved in 7.5 g of water, was added thereto. Further, an aqueous solution having 1.96 g of tetra-n-butylammonium bromide dissolved in 10 g of water, was added, and the mixture was vigorously stirred for two hours. The charged molar ratio at that time was such that  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ , and  $\text{MgO}/\text{SiO}_2 = 0.025$ , and  $\text{SiO}_2/\text{P}_2\text{O}_5 = 200$ . This gel mixture was charged into an autoclave having an internal capacity of 100 ml and subjected to hydrothermal treatment at 180°C for 48 hours under natural pressure. The product was collected by

filtration, washed with water, dried at 120°C overnight and calcinated at 550°C for 6 hours in air. 1 g of the product was mixed with 15 ml of 0.8 N hydrochloric acid, subjected to stirring treatment at room temperature for  
5 24 hours, then thoroughly washed with water, then dried at 120°C overnight and calcinated at 550°C for 6 hours in air to obtain a H-type calcium-containing crystalline porous aluminophosphosilicate. The composition of this calcium-containing crystalline porous  
10 aluminophosphosilicate was analyzed by X-ray fluorescence, and the results are shown in Table 2. 1 g of this calcium-containing crystalline porous aluminophosphosilicate was mixed with 0.36 g of calcium carbonate obtained by calcinating calcium-acetate at  
15 500°C for 10 hours and then at 550°C for 6 hours, in a mortar in a solid state, to obtain a calcium-mixed H-type calcium-containing crystalline porous aluminophosphosilicate.

TABLE 2

|                           | SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub><br>(molar ratio) | MO<br>(wt%) | MO/SiO <sub>2</sub><br>(molar ratio) | B <sub>2</sub> O <sub>3</sub><br>(wt%) | SiO <sub>2</sub> /B <sub>2</sub> O <sub>3</sub><br>(molar ratio) | P <sub>2</sub> O <sub>5</sub><br>(wt%) | SiO <sub>2</sub> /P <sub>2</sub> O <sub>5</sub><br>(molar ratio) |
|---------------------------|-------------------------------------------------------------------|-------------|--------------------------------------|----------------------------------------|------------------------------------------------------------------|----------------------------------------|------------------------------------------------------------------|
| Preparation<br>Example 1  | 323                                                               | -           | -                                    | -                                      | -                                                                | -                                      | -                                                                |
| Preparation<br>Example 4  | 53                                                                | 14.0        | 0.27                                 | -                                      | -                                                                | -                                      | -                                                                |
| Preparation<br>Example 5  | 110                                                               | -           | -                                    | 0.88                                   | 129                                                              | -                                      | -                                                                |
| Preparation<br>Example 6  | 382                                                               | 0.4         | 0.004                                | -                                      | -                                                                | -                                      | -                                                                |
| Preparation<br>Example 8  | 285                                                               | 0.1         | 0.002                                | -                                      | -                                                                | -                                      | -                                                                |
| Preparation<br>Example 12 | 271                                                               | 1.2         | 0.015                                | -                                      | -                                                                | -                                      | -                                                                |
| Preparation<br>Example 13 | 527                                                               | 0.4         | 0.004                                | -                                      | -                                                                | 0.07                                   | 3040                                                             |

M: Metal

## REACTION

For the reaction, an atmospheric pressure fixed bed flow reaction apparatus was used, and a mixture comprising 0.1 g of the crystalline porous aluminosilicate obtained in Preparation Example 1 (Example 2), or 0.136 g of the crystalline porous aluminosilicate or crystalline porous aluminoborosilicate modified with metal elements, obtained in one of Preparation Examples 2 to 13 (Examples 3 to 14), as a solid acid catalyst, and 0.5 g of quartz sand as a diluent, was packed in a reaction tube made of PYREX (registered trademark) and having an outer diameter of 6 mm, and a reaction was carried out under the reaction conditions as shown in Table 3. The reaction results were analyzed by means of gas chromatography, and the results are shown in Table 3.

TABLE 3

|        | Reaction conditions    |                 |                                 |                                    |                              |                                             |                |
|--------|------------------------|-----------------|---------------------------------|------------------------------------|------------------------------|---------------------------------------------|----------------|
|        | Catalyst               | Methanol (mol%) | Ethylene/methanol (molar ratio) | Methanol WHSV ( $\text{hr}^{-1}$ ) | Water/methanol (molar ratio) | Reaction temperature ( $^{\circ}\text{C}$ ) | Reaction time  |
| Ex. 2  | Preparation Example 1  | 6.5             | 5                               | 0.5                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 3  | Preparation Example 2  | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 4  | Preparation Example 3  | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 5  | Preparation Example 4  | 6.5             | 5                               | 0.1                                | 4                            | 450                                         | 40 min<br>8 hr |
| Ex. 6  | Preparation Example 5  | 6.5             | 5                               | 0.1                                | 4                            | 430                                         | 40 min<br>8 hr |
| Ex. 7  | Preparation Example 6  | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 8  | Preparation Example 7  | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 9  | Preparation Example 8  | 6.5             | 5                               | 0.5                                | 4                            | 400                                         | 40 min<br>7 hr |
| Ex. 10 | Preparation Example 9  | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 11 | Preparation Example 10 | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 12 | Preparation Example 11 | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 13 | Preparation Example 12 | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |
| Ex. 14 | Preparation Example 13 | 6.5             | 5                               | 0.4                                | 4                            | 400                                         | 40 min<br>8 hr |

TABLE 3 (continued)

|        | Reaction results        |                                                                             |           |        |                                           |
|--------|-------------------------|-----------------------------------------------------------------------------|-----------|--------|-------------------------------------------|
|        | Methanol conversion (%) | Hydrocarbon composition in the component discharged from the reactor (mol%) |           | Butene | Yield of propylene to methanol fed (mol%) |
|        |                         | Ethylene                                                                    | Propylene |        |                                           |
| Ex. 2  | 100                     | 66.3                                                                        | 12.8      | 8.7    | 54.8                                      |
|        | 100                     | 88.3                                                                        | 6.1       | 2.6    | 30.4                                      |
| Ex. 3  | 100                     | 50.2                                                                        | 13.7      | 13.4   | 50.8                                      |
|        | 100                     | 71.0                                                                        | 10.6      | 8.2    | 45.9                                      |
| Ex. 4  | 100                     | 21.2                                                                        | 14.6      | 15.9   | 44.3                                      |
|        | 100                     | 68.3                                                                        | 11.5      | 9.1    | 48.9                                      |
| Ex. 5  | 100                     | 38.1                                                                        | 21.2      | 15.3   | 73.5                                      |
|        | 100                     | 45.8                                                                        | 19.8      | 14.4   | 72.9                                      |
| Ex. 6  | 100                     | 38.5                                                                        | 24.0      | 15.8   | 85.7                                      |
|        | 100                     | 34.1                                                                        | 24.1      | 16.8   | 82.6                                      |
| Ex. 7  | 100                     | 14.1                                                                        | 14.6      | 14.3   | 39.5                                      |
|        | 100                     | 46.3                                                                        | 16.4      | 13.1   | 58.3                                      |
| Ex. 8  | 100                     | 16.6                                                                        | 14.5      | 14.8   | 13.7                                      |
|        | 100                     | 45.8                                                                        | 17.1      | 14.1   | 60.8                                      |
| Ex. 9  | 100                     | 49.8                                                                        | 22.3      | 12.1   | 85.0                                      |
|        | 100                     | 72.8                                                                        | 13.2      | 5.9    | 58.8                                      |
| Ex. 10 | 100                     | 55.3                                                                        | 21.1      | 10.4   | 84.0                                      |
|        | 100                     | 73.7                                                                        | 12.9      | 5.9    | 57.7                                      |
| Ex. 11 | 100                     | 53.4                                                                        | 22.4      | 10.6   | 88.2                                      |
|        | 100                     | 71.9                                                                        | 13.8      | 5.9    | 61.2                                      |
| Ex. 12 | 100                     | 31.9                                                                        | 24.7      | 14.3   | 81.6                                      |
|        | 100                     | 59.2                                                                        | 18.0      | 9.0    | 73.0                                      |
| Ex. 13 | 100                     | 24.0                                                                        | 21.2      | 12.6   | 65.3                                      |
|        | 100                     | 67.1                                                                        | 15.7      | 7.0    | 67.8                                      |
| Ex. 14 | 100                     | 39.6                                                                        | 21.3      | 15.0   | 73.8                                      |
|        | 100                     | 80.3                                                                        | 9.5       | 4.6    | 44.3                                      |

As is evident from the results shown in Table 3, as compared with the case of Example 2 wherein a non-modified crystalline porous silicate was used as a solid acid catalyst, in the case of Example 3 or 4 wherein a crystalline porous silicate modified with calcium or strontium was used, the yield of propylene to methanol fed shows a high yield even after 8 hours of the reaction time against after 40 minutes of the reaction time, and the difference in yield between the two reaction times is -4.9% or +4.6%, respectively, while in Example 2, the yield is low and decreased by -24.4% between the two reaction times. Namely, it is evident that according to the process of the present invention, a high yield can be accomplished, and at the same time a decrease in yield for an operation for a long time can be suppressed. Further, as shown in Examples 5 to 12, it is evident that also in the case wherein a crystalline porous silicate modified with other metal elements is used as a solid acid catalyst, a high yield can be accomplished, and at the same time, a decrease in yield of propylene in an operation for a long time can be suppressed.

#### EXAMPLE 15

##### PREPARATION OF CATALYST

MCM22 precursor: 0.8 g of 70%  $\text{NaAlO}_2$  and 1.4 g of NaOH were dissolved and stirred in 162 g of deionized water. When a transparent aqueous solution was obtained, 9.9 g of hexamethyleneimine and 12 g of silica (AEROSIL

200, by NIPPON AEROSIL CO., LTD.) were added, followed by stirring for two hours. The obtained slurry was divided into two 100 ml autoclaves and subjected to tumbling at 150°C for 7 days. The autoclaves were cooled and then, the contents were collected by filtration, washed with water and dried at 120°C to obtain MCM22 precursor.

ITQ-2: 4.5 g of MCM22 precursor was added to an aqueous solution having 5.1 g of hexadecyltrimethylammonium bromide and 5.5 g of 40% of tetrapropylammonium hydroxide dissolved in 12.4 g of water, followed by refluxing at 80°C for 16 hours. The obtained slurry was treated for one hour with ultrasonic waves. Then, a 0.25 M hydrochloric acid solution was dropwise added to bring the pH to at most 2, followed by filtration, washing with water, then drying and calcination at 550°C for 24 hours, to obtain a ITQ-2, which was used as a catalyst.

#### REACTION

A reaction was carried out in the same manner as in Example 2 except that 0.1 g of ITQ-2 obtained in the above method was used as the catalyst. Gas chromatography was employed for the analysis of the product. The reaction results after 40 minutes and after 8 hours from the initiation of the reaction are shown in Table 4.

TABLE 4

|                                                     |           | Ex. 15 |      | Ex. 2 |      |
|-----------------------------------------------------|-----------|--------|------|-------|------|
| Catalyst                                            |           | ITQ-2  |      | ZSM-5 |      |
| Reaction time (min)                                 |           | 40     | 480  | 40    | 480  |
| Methanol conversion (%)                             |           | 100    | 100  | 100   | 100  |
| Hydrocarbon composition in the reaction product (%) | Ethylene  | 18.6   | 19.3 | 66.3  | 88.3 |
|                                                     | Propylene | 9.6    | 15   | 12.8  | 6.1  |
|                                                     | Butene    | 9.1    | 15.5 | 8.7   | 2.6  |
| Yield of propylene to methanol fed (%)              |           | 29.3   | 48.7 | 54.8  | 30.4 |
| Change in yield of propylene (%/hr)                 |           | 2.7    |      | -3.3  |      |

As is evident from the results shown in Tale 4, when ITQ-2 being lamellar zeolite, is employed, the change in  
 5 yield of propylene from after 40 minutes to after 8 hours is 2.7, and thus, even in a reaction for a long time, both the conversion of methanol as the reaction substrate and the yield of propylene can be maintained at high levels. Whereas, when ZSM-5 is employed, the change in  
 10 yield of propylene from after 40 minutes to after 8 hours, is -3.3, and the yield of propylene decreases as the time passes, although after 40 minutes, both the conversion and the yield of propylene show high levels.

Namely, it is evident that in Example 2, due to the  
 15 decrease in the catalytic activities, it was not possible to use the catalyst for a long period of time, while in Example 15, the yield of propylene does not decrease, and propylene can be obtained constantly.

The entire disclosures of Japanese Patent Application  
 20 No. 2003-415367 filed on December 12, 2003, Japanese

Patent Application No. 2004-45917 filed on February 23,  
2004, Japanese Patent Application No. 2004-45918 filed on  
February 23, 2004, Japanese Patent Application No. 2004-  
45919 filed on February 23, 2004, Japanese Patent  
5 Application No. 2004-101075 filed on March 30, 2004,  
Japanese Patent Application No. 2004-134145 filed on  
April 28, 2004 and Japanese Patent Application No. 2004-  
153547 filed on May 24, 2004 including specifications,  
claims and summaries are incorporated herein by reference  
10 in their entireties.

## CLAIMS

1. A process for producing propylene which comprises bringing ethylene in contact with methanol and/or dimethyl ether in the presence of a catalyst and which is  
5 characterized in that the amount of ethylene in a reaction mixture being discharged from the reaction system is reduced as compared with the amount of ethylene being fed to the reaction system, and that propylene is obtained in a yield of at least 40 mol% based on the sum  
10 of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system.
2. The process for producing propylene according to Claim 1, characterized in that the reaction pressure is  
15 adjusted within a range of at least 0.1 kPa and less than 2 MPa so as to reduce the amount of ethylene in a reaction mixture being discharged from the reaction system as compared with the amount of ethylene being fed to the reaction system and to bring the yield of  
20 propylene to be at least 40 mol% based on the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system, and that the amount of ethylene being fed to the reaction system is adjusted within a range of  
25 at least 1 and at most 20 by molar ratio based on the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to

the reaction system.

3. The process for producing propylene according to Claim 1, characterized in that the weight hourly space velocity per weight of a catalytically active component, of the sum of methanol and dimethyl ether calculated as methanol, which are being fed to the reaction system, is adjusted within a range of at least  $0.01 \text{ hr}^{-1}$  and at most  $70 \text{ hr}^{-1}$  so as to reduce the amount of ethylene in a reaction mixture being discharged from the reaction system as compared with the amount of ethylene being fed to the reaction system and to bring the yield of propylene to be at least 40 mol% based on the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system.

4. The process for producing propylene according to any one of Claims 1 to 3, characterized in that the amount of ethylene being fed to the reaction system is at least 1.8 by molar ratio based on the sum of the number of moles of methanol and two times the number of moles of dimethyl ether which are being fed to the reaction system.

5. The process for producing propylene according to any one of Claims 1 to 4, characterized in that the catalyst is a solid acid catalyst.

6. The process for producing propylene according to Claim 5, characterized in that the solid acid catalyst is a zeolite.

7. The process for producing propylene according to Claim 6, characterized in that the zeolite is a crystallizable porous silicate modified with a metal element of Groups 1 to 14 of the Periodic Table other than a silicon element and an aluminum element, or a  
5 crystallizable porous aluminophosphate likewise modified.
8. The process for producing propylene according to Claim 5, wherein the solid acid catalyst is a lamellar zeolite.
- 10 9. The process for producing propylene according to any one of Claims 1 to 8, characterized in that water is fed to the reaction system.
10. The process for producing propylene according to any one of Claims 1 to 9, wherein the ethylene is ethylene  
15 obtained by a facility for the production of olefins by thermal decomposition of naphtha.
11. The process for producing propylene according to any one of Claims 1 to 9, wherein the ethylene is ethylene obtained by a facility for the production of lower  
20 olefins using methanol and/or dimethyl ether as raw materials.
12. The process for producing propylene according to any one of Claims 1 to 9, wherein the ethylene is ethylene obtained by a facility for the production of ethylene by  
25 steam cracking of ethane.