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(54) **Title:** HYDROCARBON STEAM CRACKING CATALYST FOR OLEFIN PREPARATION, METHOD FOR PREPARING THE SAME, AND OLEFIN PREPARATION METHOD USING THE SAME

(57) **Abstract:** The present invention relates to a catalyst for steam cracking of hydrocarbons, which steam cracks hydrocarbons to improve a yield of olefins such as ethylene and propylene, reduces produced coke, and has superior thermal stability at a high temperature. Particularly, the present invention provides a catalyst for steam cracking of hydrocarbons comprising potassium phosphate as a catalyst component, preparation thereof, and olefin preparation by steam cracking of hydrocarbons using the same.

HYDROCARBON STEAM CRACKING CATALYST FOR OLEFIN

PREPARATION, METHOD FOR PREPARING THE SAME, AND OLEFIN

PREPARATION METHOD USING THE SAME

BACKGROUND OF THE INVENTION

5   **(a) Field of the Invention**

The present invention relates to a catalyst for preparing ethylene and propylene, particularly to a catalyst for steam cracking of hydrocarbons that can steam crack hydrocarbons to improve yield when preparing olefins such as ethylene and propylene, reduce generated coke, and that has superior thermal

10   stability at a high temperature, and preparation thereof, and a method for preparing olefins using the same.

(b) Description of the Related Art

Ethylene and propylene are important basic raw materials for petrochemicals. They are prepared by thermal cracking hydrocarbons having

15   paraffin compounds as main ingredients, such as natural gas, naphtha, gasoil, etc. in the presence of steam at a high temperature of 800°C or more. In order to increase yields of ethylene and propylene in hydrocarbon steam cracking, the conversion rate of hydrocarbons should increase, or the selectivity of olefins should increase. However, because increasing the conversion rate of

20   hydrocarbons or the selectivity of olefins by steam cracking only is limited, various methods for increasing olefin yield have been suggested.

As a method for improving ethylene and propylene yield in hydrocarbon steam cracking, steam cracking using a catalyst has been suggested. U.S.P.

No. 3,644,557 has disclosed using a catalyst consisting of magnesium oxide and zirconium oxide, U.S.P. No. 3,969,542 disclosed a catalyst having calcium aluminate as a basic ingredient, U.S.P. No. 4,111,793 disclosed a manganese oxide catalyst supported in zirconium oxide, E.P. No. 0212320 disclosed a ferrous catalyst supported in magnesium oxide, and U.S.P. No. 5,600,051 disclosed a catalyst consisting of barium oxide, alumina, and silica. However, these catalysts have problems of serious catalyst coking during hydrocarbon steam cracking.

Decomposition of hydrocarbons at high temperatures generates substantial amounts of coke. In order to remove such coke, steam is used as a reactant-diluting agent, but significant coking still occurs and it is accumulated on reactor wall surfaces, etc. and causes many problems.

Specifically, coke accumulated on the wall surface of a thermal cracking reaction tube increases heat transfer resistance, which decreases the amount of heat transferred to the hydrocarbons. When heat transfer resistance increases, the reactor temperature must be increased in order to provide a heat quantity that is sufficient for reaction, which shortens the life of the reactor. Additionally, coke accumulated on the surface of the reactor wall reduces the effective cross section of the reactor, increasing the differential pressure of the reactor, and consequently more energy is required for compressing and injecting reactant.

As explained, in steam cracking of hydrocarbons, coke increases heat transfer resistance or differential pressure, which makes normal operation of the reactor impossible, and thus the operation of the reactor must be interrupted in order to remove the coke. Particularly, if a catalyst is used in hydrocarbon steam cracking, coke is accumulated on the surface of the catalyst as well as on

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the wall surface of the reactor, which may cause more serious problems.

Accumulation of coke on the catalyst surface lowers the catalyst performance, as well as rapidly increases differential pressure on the catalyst layer, and thus in order to normally operate the reactor, the reactor operation must be interrupted more frequently. Since the catalyst surface has a function for collecting-condensing coke precursors produced in the gas phase, and it may have an activity for promoting coke production according to catalyst components, a catalyst for hydrocarbon steam cracking should have properties for preventing coking to the highest degree. Generally, in commercial steam-cracking reactors, coke is removed with a cycle of 30 to 60 days, and for this, operation of the reactor is interrupted and the coke is burned to remove it while drawing off fumes under a steam atmosphere. The time required for removing coke varies according to the amount of coke accumulated on the reactor, and generally 1 to 2 days are required. However, if a catalyst having insufficient coke-removal performance is used and thus the coke-removal cycle is substantially shortened, even if the use of a catalyst increases ethylene and propylene yields, ethylene and propylene production amounts per unit period may decrease compared to the pure thermal cracking process, and expenses for coke-removal may increase. Therefore, in order to bring about economic efficiency in a process using a catalyst in hydrocarbon steam cracking, a catalyst that can minimize catalyst coking and prolong the coke-removal cycle is required.

As a method for reducing coke generation, a method for gasifying coke to remove it has been suggested. U.S.P. No. 3,872,179 suggested a catalyst in which an alkali metal oxide is added to a zirconium catalyst, and Russian Patent No. 1,011,236 suggested a potassium vanadate catalyst in which boron oxide is

supported on an alumina carrier.   Since such alkali metal oxide and potassium vanadate compounds gasify produced coke into COx, they are very effective in coke removal, and coke removal performance can be improved by increasing a supported amount and thus the coke removal cycle can be prolonged

5   correspondingly.

However, the loss of alkali metal oxide or potassium vanadate catalyst inevitably occurs at a high temperature to crack hydrocarbons.   Specifically, they are likely to exist in a liquid phase in a thermal cracking reactor at a high temperature due to a low melting point of the catalyst components, and the

10   catalyst components are evaporated because of a rapid reactant gas flow, which causes a loss as the reaction proceeds.   This shortens the life cycle of the catalyst, and in order to compensate for such a loss of catalyst, catalyst components are added during reaction.   In order to give economical efficiency to thermal cracking and avoid a complicated process, a catalyst having superior

15   thermal stability at a high temperature is required.

SUMMARY OF THE INVENTION

The present invention is made in consideration of the problems of the prior art, and it is an object of the present invention to provide a catalyst for steam cracking of hydrocarbons that steam cracks hydrocarbons to improve

20   yield when preparing olefins such as ethylene and propylene, and simultaneously reduces produced coke, and has superior coke-removal performance and thermal stability at a high temperature, and preparation thereof, and a method for preparing olefins by hydrocarbon steam cracking using the same.

25   In order to achieve these objects, the present invention provides a

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catalyst for steam cracking of hydrocarbons comprising potassium phosphate as a catalyst component.

The present invention also provides a process for preparing a catalyst for steam cracking of hydrocarbons comprising the steps of:

5   a) dissolving potassium phosphate or a precursor thereof in water to prepare an aqueous solution of potassium phosphate precursor; and

b) impregnating a carrier in the a) aqueous solution to prepare a supported catalyst.

The process may further comprise a step of c) calcination the b) 10   supported catalyst.

The present invention also provides a process for preparing a catalyst for steam cracking of hydrocarbons comprising the steps of

a) mixing potassium phosphate or a potassium phosphate precursor powder and a metal oxide powder; and

15   b) calcination the mixture to prepare a calcined catalyst of potassium phosphate-metal oxide.

The present invention also provides a process for preparing olefins by steam cracking of hydrocarbons comprising the step of steam cracking hydrocarbons in the presence of a catalyst comprising potassium phosphate as a 20   catalyst component.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows results of combustion tests of Comparative Example 4 and Example 10, using a thermogravimetric analyzer.

DETAILED DESCRIPTION AND THE PREFERRED EMBODIMENTS

25   The present invention will now be explained in detail.

5

General hydrocarbon steam cracking prepares ethylene, propylene, etc. by steam cracking reactants at a high temperature of 800 ℃ or more without a catalyst, using natural gas, naphtha, gasoil, etc. as a reactant. The present invention is based on the discovery that when using potassium phosphate as a catalyst component in such steam cracking, ethylene and propylene yields can increase compared to conventional steam cracking, and performance of removing coke produced in a catalyst during thermal cracking as well as thermal stability of the catalyst are superior.

The catalyst of the present invention for steam cracking of hydrocarbons, comprising potassium phosphate as a catalyst component, can be used in three forms. One is potassium phosphate itself, another is a supported catalyst in which potassium phosphate is supported in a carrier, and the next is a calcined catalyst in which a mixture of potassium phosphate and metal oxide is calcined.

Potassium phosphate used as an active ingredient in the present invention efficiently removes coke, and has a high melting point and thus is very stable at high temperatures where steam cracking of hydrocarbons occurs. Conventionally used catalysts, if they have superior coke-removal performance, produce excessive COx or they are inferior in stability at high temperatures to cause loss of active material. Meanwhile, since the catalyst of the present invention uses potassium phosphate that has very high melting point and simultaneously has superior coke-removal performance, loss of the active ingredient potassium phosphate does not occur while it significantly decreases the amount of coke accumulated in the catalyst.

In the supported catalyst in which potassium phosphate is supported on a carrier, one of the forms of the catalyst of the present invention, it is preferable

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in terms of hydrocarbon steam cracking that, on the basis of total supported

catalyst weight, 0.5 to 50 wt% of potassium phosphate is supported.   If less

than 0.5 wt% of potassium phosphate is supported, it is difficult to show catalyst

performance, and if it exceeds 50 wt%, effects are not in proportion to the

5   supported amount.

As a carrier, common carriers such as α-alumina, silica, silica-alumina,

zirconium oxide, magnesium oxide, magnesium aluminate, calcium aluminate,

and zeolite can be used.   Preferably, a carrier having a surface area of 0.1 m^2/g

or less is used.

10   The supported catalyst is prepared by dissolving a potassium phosphate

precursor of a potassium phosphate salt such as potassium phosphate or

potassium phosphate hydrate ($K_3PO_4 \cdot nH_2O$), or a salt of potassium hydroxide

and ammonium phosphate, in water, to prepare an aqueous solution thereof,

impregnating the aqueous solution in α-alumina by an initial impregnation

15   method or a liquid impregnation method, and drying at 120 ℃ for 10 hours or

more.   Additionally, a carrier in which potassium phosphate is impregnated may

be calcined at a high temperature so that the potassium phosphate may be firmly

fixed.   Calcination is preferably conducted at 750 to 1500 ℃ for 4 hours or

more.   If calcination at more than 1500 ℃, potassium phosphate may be

20   evaporated and lost.

In addition, a calcined catalyst in which a mixture of potassium

phosphate and a metal oxide is calcined, one of the forms of the catalyst of the

present invention, is prepared by physically mixing a potassium phosphate

precursor powder of a potassium phosphate salt such as potassium phosphate

powder or potassium phosphate hydrate ($K_3PO_4 \cdot nH_2O$), or a salt of potassium

hydroxide and ammonium phosphate, with metal oxides such as α-alumina,

silica, silica-alumina, zirconium oxide, magnesium oxide, magnesium aluminate,

potassium aluminate, or zeolite, and then calcination it at a high temperature and

5   forming it into a regular shape.   Calcination is preferably conducted at 400 to

1500 ℃.   If calcination at more than 1500 ℃, the potassium phosphate may be

evaporated and lost.   The contents of potassium phosphate required for

hydrocarbon steam cracking are preferably 0.5 to 50 wt% in the calcined catalyst.

If less than 0.5 wt% of potassium phosphate are contained, it is difficult to show

10   catalyst performance, and if more than 50 wt% are contained, effects are not

proportional to the contents.

The process for preparing various olefins by hydrocarbon steam cracking

comprises the step of steam cracking various hydrocarbons in the presence of a

catalyst comprising potassium phosphate as a catalyst component.   The steam

15   cracking is conducted under common steam cracking conditions.   For examples,

steam cracking is conducted at a reaction temperature of 600 to 1000 ℃, at a

weight ratio of steam/hydrocarbons of 0.3 to 1.0, and at an LHSV (liquid hourly

space velocity) of 1 to 20 hr^{-1}, in the presence of a catalyst for hydrocarbon

steam cracking to prepare olefins.

20   In applying the hydrocarbon steam cracking, applicable reactors include

a fixed bed reactor, a fluidized bed reactor, a moving bed reactor, etc.

Generally, in a reaction process repeatedly recycling a catalyst within a short

period such as a fluidized bed reactor or a moving bed reactor, if α-alumina

itself is used as a catalyst, the catalyst particles function as a heat transfer

medium to increase the hydrocarbon conversion rate, thereby increasing the

ethylene and propylene yield.   Particularly, if the potassium phosphate catalyst

component of the present invention is supported or contained in such a catalyst,

less coke is produced compared to conventional catalysts (or solid heat medium)

5   and there is no loss of catalyst component, so it is very economical.

In the case hydrocarbon steam cracking is proceeded in a fixed bed

reactor, it is preferable to use a supported catalyst in which potassium phosphate

is supported in α-alumina.   A catalyst used in the fixed bed reactor may be

formed into circle or pellet shapes, but in this case, differential pressure falls a

10   great deal on the catalyst layer, and thus in order to solve this problem, it is

preferable to form a catalyst in a lasik ring shape or other special shapes so as

to increase porosity of the catalyst layer as much as possible.

When the catalyst of the present invention comprising potassium

phosphate as a catalyst component is used when preparing various olefins by

15   hydrocarbon steam cracking, a high yield of olefins such as ethylene and

propylene can be obtained, and the amount of coke produced during reaction

can be reduced and the loss of the catalyst component at a high temperature

can be minimized.   Additionally, after hydrocarbon thermal cracking is

completed, coke accumulated in the catalyst is easily removed even at a low

20   temperature during a catalyst regeneration process of removing coke produced

in the catalyst.   Specifically, coke produced in the catalyst comprising potassium

phosphate in hydrocarbon steam cracking can be easily removed by heating at

500 to 1300 ℃ in the presence of air, air and steam, or steam.

Therefore, the catalyst according to the present invention can largely

25   improve ethylene and propylene yield compared to conventional steam cracking,

largely reduce the amount of coke accumulated on a catalyst during hydrocarbon

cracking, and it has superior thermal stability and thus loss of the catalyst

component can be prevented.   In addition, since coke removal can be

conducted at a low temperature during a regeneration process of the catalyst,

5   the life cycle of the catalyst can increase, and the catalyst activity is superior

when repeatedly using it.

The present invention will be explained in more detail with reference to

the following Examples.   However, these are to illustrate the present invention

and the present invention is not limited to them.

10   [Examples]

Comparative Examples 1~2 and Examples 1~4

As a carrier for preparing a catalyst, α-alumina is used.   The α-

alumina is spherical with a diameter of 5 mm, and has a surface area of 0.04

m^2/g, porosity of 21.89%, and an average pore diameter of 19.76 mm.

15   In order to prepare a catalyst of Comparative Examples 1~2 using the

alumina carrier, as shown in Table 2, 4.06 g of potassium hydroxide, a precursor

of potassium vanadate, 8.48 g of ammonium vanadate, and 3.54 g of boron acid

were dissolved in 15 to 50 g of water according to the porosity of the α-alumina

to prepare an aqueous solution.   The aqueous solution was supported in 100 g

20   of alumina by an incipient wetness method.   The catalyst in which the catalyst

precursor aqueous solution was impregnated in α-alumina was dried in an oven

at 110 ℃ under an air atmosphere for 10 hours or more, and then transferred to

a furnace to calcine at 750 ℃ for 4 hours.   The catalysts calcined according to

the above-explained process commonly have 10 wt% of potassium vanadate

and 2 wt% of boron oxide, on the basis of the weight of the α-alumina.

Additionally, in order to prepare catalysts of Examples 1~4 using the alumina carrier, as shown in Table 2, 10.8 to 16.2 g of potassium phosphate hydrate ($K_3PO_4 \cdot 1H_2O$), a precursor of potassium phosphate, were dissolved in

5   15 to 50 g of water according to the porosity of the α-alumina to prepare an aqueous solution thereof, and then the aqueous solution was supported on 100 g of the alumina carrier by an incipient wetness method. The impregnated catalyst was dried in an oven at 110 ℃ for 10 hours or more, and then transferred to a calcination furnace to fire at 750 to 1000 ℃ for 4 hours. The

10   catalyst calcined according to the above-explained process has 10 to 15 wt% of potassium phosphate, on the basis of the weight of the α-alumina.

Using each of the prepared catalysts, ethylene and propylene were prepared by the following method. In steam cracking of hydrocarbons, naphtha was used for the hydrocarbons and the composition and physical properties of

15   the naphtha used are as shown in Table 1.

[Table 1]

Physical properties			Composition (wt%)			
Density (g/cc)	Initial boiling point (℃)	Final boiling point (℃)	n-paraffin	I-paraffin	naphthene	aromatic
0.675	30.9	160.7	39.5	38.9	15.3	6.3

The reactants naphtha and water were injected into a reactor with a metering pump, with the injection ratio of naphtha and water controlled to a

20   weight ratio of 2 : 1 and the flow rate of naphtha controlled so that the LHSV became 10 hr^{-1}. Before the naphtha and water were injected into the reactor, they were respectively passed through a vaporizer and mixed, the mixture was

passed through a first preheater and heated to 550 ℃, then through a second

preheater to be heated to 650 ℃, and finally it was injected into a quartz reactor

filled with a catalyst (length: 45 cm; diameter: 3/8 inches).

The reactor was heated to 880 ℃ by an electrical furnace consisting of

5   3 stages, and contact thermal cracking occurred while the steam-naphtha

mixture, having passed through the second preheater, passed through the

reactor. While the reaction product passed through two condensers connected

in series, water and heavy oil were condensed and separated as a liquid phase,

and the remaining gas-phase mixture was analyzed by gas chromatography on-

10   line and then discharged. The ethylene yield was calculated by the following

Mathematical Formula 1, and the yield of the other product (propylene) was

calculated by the same method.

[Mathematical Formula 1]

Ethylene yield (wt%) = ethylene production amount / naphtha injection amount

15   x 100

In the following Table 2, results of catalytic cracking and pure steam

cracking of naphtha are shown. After the reaction was completed, the catalyst

layer was separated into upper, middle, and lower stages, and the catalyst was

taken from the lower stage where the most coke was produced and the amount

20   of coke produced in the catalyst was measured. Ethylene and propylene yields

are shown as wt% on the basis of the amount of naphtha injected during a 4

hour reaction, and the amount of coke is shown as wt% on the basis of the

weight of the catalyst taken after the reaction.

[Table 2]

	Comparative Example 1	Comparative Example 2	Example 1	Example 2	Example 3	Example 4
Catalyst composition	Catalyst-free thermal cracking	KVO_3 10 wt% B_2O_3 2 wt%	K_3PO_4 10 wt%	K_3PO_4 10 wt%	K_3PO_4 15 wt%	K_3PO_4 15 wt%
Carrier	-	alumina	Alumina	alumina	alumina	alumina
Calcination temperature (℃)	-	750	750	1000	750	1000
Ethylene yield (wt%)	·23.9	31.1	31.6	31.2	31.4	31.2
Propylene yield (wt%)	12.8	17.3	17.2	17.2	17.2	17.2
Coke produced in catalyst after reaction (wt%)	-	7.64	6.04	6.76	2.8	4.0

As shown in Table 2, ethylene and propylene products of Examples 1~4 using the potassium phosphate catalyst component were much higher than those of Comparative Example 1 in which naphtha was thermally cracked without using a catalyst. Additionally, the amount of coke produced in the catalyst of Examples 1~4 using the potassium phosphate catalyst component substantially decreased by 20 to 64 % based on that of Comparative Example 2 using potassium vanadate and boron oxide as catalyst components.

Examples 5~7

In order to prepare catalysts of Examples 5~7, the same α -alumina carrier as used in Comparative Example 2 and Examples 1~4 was used. As a precursor of potassium phosphate, 7.89 to 11.8 g of potassium hydroxide (KOH) and 5.44 to 8.16 g of ammonium phosphate salt $(NH_4)H_2PO_4)$ were dissolved in water to prepare an aqueous solution, and then the aqueous solution was supported on 100 g of a carrier by an incipient wetness method.

The supported catalyst was dried in an oven of 110 ℃ for 10 hours or

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more, and then transferred to a furnace to calcine at 750 to 1000 ℃ for 4 hours.

The catalyst calcined according to the above-explained process has 10 to 15

wt% of potassium phosphate on the basis of the weight of α-alumina.

Hydrocarbon steam cracking of the prepared catalyst was conducted by the

5   same process as in Examples 1~4, and the results are as shown in Table 3.

[Table 3]

	Comparative Example 1	Comparative Example 2	Example 5	Example 6	Example 7
Catalyst composition	Catalyst-free thermal cracking	KVO₃ 10 wt% B₂O₃ 2 wt%	K₃PO₄ 10 wt%	K₃PO₄ 10 wt%	K₃PO₄ 15 wt%
Carrier	-	alumina	alumina	alumina	alumina
Calcination temperature	-	750	750	1000	750
Ethylene yield (wt%)	23.9	31.1	31.5	31.2	31.0
Propylene yield (wt%)	12.8	17.3	17.1	17.1	17.5
Coke produced in the catalyst after reaction (wt%)	-	7.64	5.91	6.39	1.8

As shown in Table 3, even if the precursor is changed when preparing a

10   catalyst comprising potassium phosphate, ethylene and propylene products of

Examples 5~7 substantially increase compared to thermal cracking of

Comparative Example 1. Additionally, compared to Comparative Example 2

using potassium vanadate and boron oxide as catalyst components, Examples

5~7 showed similar ethylene and propylene yields, but the amount of coke

15   produced in the catalysts substantially decreased, by 23 to 77 % based on that

of comparative example.

Comparative Example 3, Examples 8~9

One of the disadvantages of a catalyst in which potassium vanadate and

boron oxide are supported is that the catalyst component is lost during thermal

cracking at a high temperature.   In order to measure the loss of catalyst

component, each of the catalysts were placed in a reactor at 880 ℃ while

injecting 2.8 g of steam per minute therein, and the amount of catalyst

component was measured after 10 hours.   The amount of loss of each catalyst

5   compared to the initial catalyst component is shown in Table 4 as wt%.

[Table 4]

		Comparative Example 2	Example 8	Example 9
Catalyst component		KVO_3 / B_2O_3	K_3PO_4	K_3PO_4
carrier		alumina	alumina	alumina
Calcination temperature(℃)		750	750	1000
Loss amount (wt%)	K	20	0	0
	V	20	-	-
	B	96	-	-

As shown in Table 4, in Comparative Example 3 using potassium

10   vanadate and boron oxide as catalyst components, with steam treating at 880 ℃

for 10 hours, the loss of potassium and vanadium was about 20 wt%, and almost

all the boron was lost.   Therefore, it can be seen that the catalyst consisting of

potassium vanadate and boron oxide lost a lot of catalyst components during

thermal cracking of hydrocarbons.   However, as in Examples 8 and 9, if

15   potassium phosphate is used as a catalyst component, there is little loss of

catalyst component.

Comparative Example 4, Example 10

In steam cracking of hydrocarbons using a catalyst, coke is continuously

accumulated on the wall surface of a reactor and the surface of a catalyst and

20   thus operation must be interrupted and a recycling process must be conducted.

In order to prolong the life of the catalyst, the coke should be rapidly removed at a low temperature in a catalyst recycling process, which allows the hydrocarbon cracking process to be operated again within a short time and thus is very favorable in terms of economy.

5   In Comparative Example 4 and Example 10, combustion tests were respectively conducted for the KVO3/alumina catalyst and the K3PO4/alumina catalyst on which coke was deposited, using a thermogravimetric analyzer.   The injected gas was air and the flow rate was fixed at 50 ml/min.   The results of combustion tests of Comparative Example 4 and Example 10 are shown in Fig. 1.

10   As seen from the results, coke deposited on the K3PO4/alumina catalyst of Comparative Example 10 begins to be removed at a temperature of about 100 ℃ lower than the temperature when the coke deposited on the KVO3/alumina catalyst of Comparative Example 4 begins to be removed, and the temperature at which the combustion of coke is terminated was about 100 ℃

15   lower than that of the KVO3/alumina catalyst (Comparative Example 4). Therefore, it was confirmed that a catalyst to which K3PO4 is added is also very favorable in the catalyst regeneration process.   The regeneration process can be conducted using air, or using a mixed gas of steam and air, or using only steam.

20   <u>Example 11</u>

Potassium phosphate hydrate ($K_3PO_4 \cdot 1H_2O$) powder was mixed with alumina powder used as a carrier in Example 1 at a weight ratio of 2:8, the mixture was calcined at 1300 ℃ under an air atmosphere for 24 hours, and then

it was granulized to prepare a calcined catalyst.

Using the prepared calcined catalyst, naphtha was steam cracked by the same method as in Examples 5 and 8 to prepare ethylene and propylene, and test results are shown in Table 5.

5   [Table 5]

		Comparative Example 1	Comparative Example 2	Example 11
Catalyst component		Catalyst-free thermal cracking	KVO_3 10 wt% B_2O_3 2 wt%	K_3PO_4 20 wt% Alumina 80wt%
Carrier		-	alumina	-
Calcination temperature (℃)		-	750	1300
Ethylene yield (wt%)		23.9	31.1	31.5
Propylene yield (wt%)		12.8	17.3	17.3
Coke produced in catalyst after reaction (wt%)		-	7.64	1.5
Loss (wt%)	K	-	20	0
	V	-	20	-
	B	-	96	-

According to the present invention, if olefins are prepared by steam cracking of hydrocarbons using a catalyst for hydrocarbon steam cracking comprising a potassium phosphate catalyst component, the ethylene propylene yield can be substantially increased compared to general thermal cracking. And compared to a common hydrocarbon steam cracking catalyst, the amount of coke accumulated in the catalyst can substantially decrease while maintaining similar ethylene and propylene yields, and thus the catalyst activity can be maintained for a long period and pressure decay in the thermal cracker can be reduced. In addition, since the catalyst has superior thermal stability at a high temperature, and coke is rapidly removed at a low temperature in a catalyst recycling process, life of the catalyst can be prolonged and thus operation is very favorable in terms of economy. The invention can be applied to a moving bed

or a fluidized bed reactor, as well as a fixed bed reactor.

WHAT IS CLAIMED IS:

1. A catalyst for steam cracking of hydrocarbons, comprising potassium phosphate as a catalyst component.

2. The catalyst for steam cracking of hydrocarbons according to Claim 1, wherein the catalyst is a supported catalyst in which potassium phosphate is supported on a carrier.

3. The catalyst for steam cracking of hydrocarbons according to Claim 2, wherein the carrier is selected from a group consisting of α-alumina, silica, silica-alumina, zirconium oxide, magnesium oxide, magnesium aluminate, calcium aluminate, and zeolite.

4. The catalyst for steam cracking of hydrocarbons according to Claim 2, wherein the supported catalyst comprises 0.5 to 50 wt% of supported potassium phosphate, on the basis of total weight of the supported catalyst.

5. The catalyst for steam cracking of hydrocarbons according to Claim 1, wherein the catalyst is a calcined catalyst of potassium phosphate and metal oxide.

6. The catalyst for steam cracking of hydrocarbons according to Claim 5, wherein the calcined catalyst comprises 0.5 to 50 wt% of potassium phosphate.

7. The catalyst for steam cracking of hydrocarbons according to Claim 5, wherein the metal oxide is selected from a group consisting of α-alumina, silica, silica-alumina, zirconium oxide, magnesium oxide, magnesium aluminate, calcium aluminate, and zeolite.

8. A process for preparing a catalyst for steam cracking of hydrocarbons, comprising the steps of:

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a) dissolving potassium phosphate or a potassium phosphate precursor in water to prepare an aqueous solution of a potassium phosphate precursor; and

b) impregnating the a) aqueous solution in a carrier to prepare a supported catalyst.

9. The process for preparing a catalyst for steam cracking of hydrocarbons according to Claim 8, further comprising the step of c) calcination the b) supported catalyst.

10. The process for preparing a catalyst for steam cracking of hydrocarbons according to Claim 8, wherein the a) potassium phosphate precursor is potassium phosphate hydrate or a salt of potassium hydroxide and ammonium phosphate.

11. The process for preparing a catalyst for steam cracking of hydrocarbons according to Claim 8, wherein the b) carrier is selected from a group consisting of α-alumina, silica-alumina, zirconium oxide, magnesium oxide, magnesium aluminate, calcium aluminate, and zeolite.

12. The process for preparing a catalyst for steam cracking of hydrocarbons according to Claim 9, wherein the c) calcination is conducted at 750 to 1500 ℃ for at least 4 hours.

13. A process for preparing a catalyst for steam cracking of hydrocarbons, comprising the steps of:

a) mixing potassium phosphate or a potassium phosphate precursor powder with a metal oxide power; and

b) calcination the mixture to prepare a calcined catalyst of potassium phosphate-metal oxide.

14. The process for preparing a catalyst for steam cracking of hydrocarbons according to Claim 13, wherein the a) potassium phosphate precursor is potassium phosphate hydrate or a salt of potassium hydroxide and ammonium phosphate.

15. The process for preparing a catalyst for steam cracking of hydrocarbons according to Claim 13, wherein the a) metal oxide is selected from a group consisting of α-alumina, silica, silica-alumina, zirconium oxide, magnesium oxide, magnesium aluminate, calcium aluminate, and zeolite.

16. The process for preparing a catalyst for steam cracking of hydrocarbons according to Claim 13, wherein the b) calcination is conducted at 400 to 1500 ℃.

17. A process for preparing olefins by steam cracking of hydrocarbons, comprising the step of steam cracking hydrocarbons in the presence of a catalyst comprising potassium phosphate as a catalyst component.

18. The process for preparing olefins according to Claim 17, wherein the steam cracking is conducted at a reaction temperature of 600 to 1000 ℃, at a weight ratio of steam/hydrocarbons of 0.3 to 1 and an LHSV (liquid hourly space velocity) of 1 to 20 hr^{-1}.

19. The process for preparing olefins according to Claim 17, wherein the steam cracking is conducted in a fixed bed reactor, a fluidized bed reactor, or a moving bed reactor.

20. The process for preparing olefins according to Claim 17, wherein the catalyst is a supported catalyst in which potassium phosphate is supported on a carrier.

21. The process for preparing olefins according to Claim 20, wherein the carrier is selected from a group consisting of α-alumina, silica, silica-alumina, zirconium oxide, magnesium oxide, magnesium aluminate, calcium aluminate, and zeolite.

22. The process for preparing olefins according to Claim 20, wherein the supported catalyst comprises 0.5 to 50 wt% of supported potassium phosphate, on the basis of total weight of the supported catalyst.

23. The process for preparing olefins according to Claim 17, wherein the catalyst is a calcined catalyst of potassium phosphate and a metal oxide.

24. The process for preparing olefins according to Claim 23, wherein the calcined catalyst comprises 0.5 to 50 wt% of potassium phosphate.

25. The process for preparing olefins according to Claim 23, wherein the metal oxide is selected from a group consisting of α-alumina, silica, silica-alumina, zirconium oxide, magnesium oxide, magnesium aluminate, calcium aluminate, and zeolite.

26. The process for preparing olefins according to Claim 17, wherein after the steam cracking is completed, the catalyst is regenerated by heating the catalyst, on the surface of which coke is generated, at 500 to 1300 ℃ in the presence of air, air and steam, or steam, to remove coke.

Fig 1
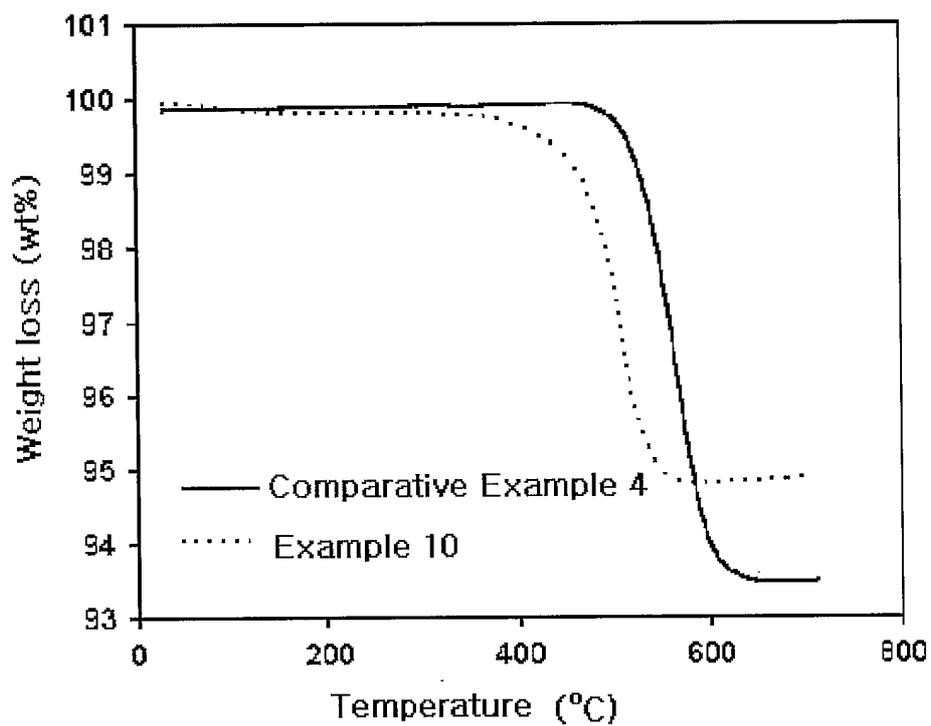
CLASSIFICATION OF SUBJECT MATTER

IPC^7: B01J 29/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC^7: B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 05038876 A1 (MOBIL OIL CORPORATION) 16 September 1992 (16.09.92) *page 4, examples 2-5; claims 1-3,7,9.*	1-26
A	EP 0252761 A2 (EXXON RESEARCH AND ENGINEERING COMPANY) 13 January 1988 (13.01.88) *page 2, lines 10-25; page 2, line 53 - page 3, line 16; page 3, lines 33-52; claims 1-8.*	1-26
A	GB 832297 A (BATAAFSCHE PETROLEUM MAATSCHAPPIJ) 6 April 1960 (06.04.60) *page 1, lines 10-13; page 1, lines 65-67; page 2, lines 29-68; page 3, lines 20-46; claim 1.*	1-26

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

Date of the actual completion of the international search	Date of mailing of the international search report
14 May 2003 (14.05.2003)	1 July 2003 (01.07.2003)

Name and mailing adress of the ISA/AT	Authorized officer
Austrian Patent Office Dresdner Straße 87, A-1200 Vienna Facsimile No. 1/53424/535	KOLLER G. Telephone No. 1/53424/458

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