

PHOSPHORUS-ALUMINA SOL, PREPARATION METHOD THEREOF, AND
USE THEREOF AS BINDER IN HYDROCARBON OIL CONVERSION
CATALYST

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the priority of patent application No. 202311436432.2 filed on October 31, 2023, entitled “A Light Olefins Additive for Promoting Heavy Oil Conversion and Preparation Method Thereof, Catalyst and Hydrocarbon Oil Catalytic Conversion Method”; patent application No. 202311435723.X filed on October 31, 2023, entitled “A Light Olefins Additive for Heavy Oil Cracking and Preparation Method Thereof, Catalyst and Use”; and patent application No. 202311435192.4 filed on November 1, 2023, entitled “A Catalytic Composition for Producing Light Olefins and Light Oil in High Yield, Preparation Method Thereof, and Hydrocarbon Oil Catalytic Conversion Method”. The contents of the above applications are incorporated herein by reference in their entirety.

TECHNICAL FIELD

The present application relates to a phosphorus-alumina sol, a preparation method thereof, and use thereof as a binder in a hydrocarbon oil conversion catalyst. The present application also relates to a hydrocarbon oil conversion catalyst, a preparation method thereof, and a hydrocarbon oil catalytic conversion method in which the catalyst is used.

BACKGROUND ART

Phosphorus-alumina sols are widely used in fields such as catalysts, building materials, refractory materials, and inorganic coatings. They are not only a binder commonly used in refractory materials but also an important component in inorganic coating formulations. Moreover, they can be used in siliceous, high-alumina, magnesia, silicon carbide, and oxide concretes. When used as a matrix in the preparation of certain catalytic cracking catalysts, they not only serve as a binder but also improve the reaction performance of the

catalyst.

In catalytic conversion processes, particularly those for converting hydrocarbon oils into low-boiling hydrocarbon products, developing a catalyst that maintains high stability while achieving high selectivity and high yield of target product(s) is a highly challenging goal. Phosphorus-alumina binders play a role in stabilizing structure, enhancing mechanical strength, and potentially participating in catalytic reactions. Molecular sieve catalysts containing a phosphorus-aluminum matrix represent a potential solution, and their research and development are of great significance for improving the efficiency and economy of the entire catalytic conversion process. However, there is very little information in the prior art about phosphorus-aluminum matrix-containing molecular sieve catalysts that are stable and selective for converting hydrocarbon molecules to produce light, light olefins. Such catalysts still struggle to meet the requirements of high hydrothermal stability, high activity and selectivity, and high conversion simultaneously.

CN1070384A provides a method for preparing a phosphorus-alumina sol: adding orthophosphoric acid or aluminum dihydrogen phosphate to an alumina sol, followed by steps such as high-temperature depolymerization and concentration to obtain the phosphorus-alumina sol. The preparation method provided by CN1070385A includes: subjecting a mixed liquid of metallic aluminum, hydrochloric acid (or aluminum chloride), and orthophosphoric acid (or aluminum dihydrogen phosphate) to a reaction under certain conditions, followed by high-temperature depolymerization and concentration to obtain a phosphorus-alumina sol.

CN1417296A provides a chlorine-free phosphorus-alumina sol usable in petroleum hydrocarbon cracking catalysts and a preparation method thereof. The preparation method includes: dispersing an acid-peptizable aluminum hydroxide or aluminum oxide with decationized water into a slurry having a solid content of 15-35 wt%, adding concentrated phosphoric acid to the slurry under stirring at a weight ratio of P/Al in a range of 1.2-6, then raising the temperature to 65-95°C and reacting at this temperature for 15-90 minutes until a transparent colloid is formed. This chlorine-free phosphorus-alumina sol can

be used in admixture with conventional chlorine-containing alumina sols.

CN102847547B discloses a phosphorus-aluminum compound-containing inorganic binder and a preparation method thereof, which includes dispersing an acid-peptizable aluminum hydroxide and/or aluminum oxide, as well as clay,
5 with decationized water into a slurry having a solid content of 15-45 wt%, adding concentrated phosphoric acid under stirring at a weight ratio of P/Al in a range of 1-6, followed by reaction at 50-99°C for 15-90 minutes.

CN115215311A provides an aluminum phosphate sol, a preparation method and use thereof, and a catalytic cracking catalyst and a preparation
10 method thereof. The aluminum phosphate sol has an outer layer structure and an internal structure inside the outer layer. The preparation method includes (1) mixing an aluminum source with water to form an aluminum source slurry; (2) bringing the aluminum source slurry obtained in step (1) into first contact with a first phosphoric acid to obtain a second slurry; (3) bringing the second
15 slurry obtained in step (2) into second contact with a second phosphoric acid, and raising the temperature for reaction.

The methods for preparing phosphorus-alumina sols provided in the prior art have problems such as high cost, complex processes, and easy solidification or precipitation of the reaction product due to fluctuations in reaction
20 conditions during preparation. The resulting phosphorus-alumina sols typically have a low degree of polymerization, e.g., less than 1, and a high content of free phosphate, making them prone to react with other alumina colloids in the catalyst and affecting binding performance. Consequently, the hydrocarbon oil conversion catalysts prepared therefrom have low activity.

25 Therefore, there is a need in the art for a phosphorus-alumina sol with a high degree of polymerization, high stability, appropriate colloidal particle size, and good binding properties, as well as high-performance hydrocarbon oil conversion catalysts based on such a phosphorus-alumina sol.

30 SUMMARY

One objective of the present disclosure is to provide a phosphorus-alumina sol binder and a preparation method thereof. The phosphorus-alumina

sol has a high degree of polymerization, high stability, appropriate colloidal particle size, and good binding properties.

Another objective of the present disclosure is to provide a hydrocarbon oil conversion catalyst prepared using the phosphorus-alumina sol, and a hydrocarbon oil catalytic conversion method using the catalyst, so as to effectively increase the yield of target products in the hydrocarbon oil catalytic conversion method, e.g., the yield of light olefins and total liquid yield, increase the olefin content in liquefied petroleum gas (LPG), reduce slurry oil and coke, promote diesel conversion, and/or reduce gasoline loss.

To achieve the above objectives, in a first aspect, the present disclosure provides a phosphorus-alumina sol, the phosphorus-alumina sol comprising Al, P, and a stabilizer, and having a P/Al weight ratio of 1.6-6 : 1; wherein the phosphorus-alumina sol exhibits a ^{31}P NMR spectrum, with the resonance signal peak area at a chemical shift of -12 ± 2 ppm designated as QP_0^2 and the resonance signal peak area at a chemical shift of 0 ± 2 ppm designated as QP_0^0 , $\text{QP}_0^2/\text{QP}_0^0 = 1.5-5$, and the phosphorus-alumina sol has an average colloidal particle size of 10-30 nm.

In a second aspect, the present disclosure provides a method for preparing the phosphorus-alumina sol according to the first aspect, comprising:

1) under stirring at a temperature of 50°C - 95°C , mixing an aluminum salt source, deionized water, and a stabilizer to form a slurry, so as to obtain an alumina precursor solution.

2) under stirring at a temperature of 25°C - 70°C , adding a phosphate to the alumina precursor solution at a P/Al weight ratio of 1.6-6 : 1 for reaction, so as to obtain the phosphorus-alumina sol.

In a third aspect, the present disclosure provides a hydrocarbon oil conversion catalyst, the catalyst comprising a molecular sieve, a phosphorus-alumina binder, other inorganic binder(s) different from the phosphorus-alumina binder, an optional metal component, an optional meso-macroporous inorganic oxide material, and an optional clay, wherein the phosphorus-alumina binder is derived from the phosphorus-alumina sol according to the first aspect or the phosphorus-alumina sol prepared by the method according

to the second aspect.

In a fourth aspect, the present disclosure provides a method for preparing the hydrocarbon oil conversion catalyst according to the third aspect, comprising:

5 a) mixing the molecular sieve, the other inorganic binder(s), a metal source of the optional metal component, the optional meso-macroporous inorganic oxide material, the optional clay, and water to form a slurry, controlling pH value of the slurry to be greater than 2.5, so as to obtain a first slurry;

10 b) mixing the first slurry with the phosphorus-alumina sol to obtain a second slurry, followed by spray drying and calcination, so as to obtain the catalyst.

In a fifth aspect, the present disclosure provides a catalyst composition, the catalyst composition comprising a cocatalyst and an optional procatalyst, 15 wherein the cocatalyst is the hydrocarbon oil conversion catalyst according to the third aspect, and the optional procatalyst preferably is a catalytic cracking catalyst.

In a sixth aspect, the present disclosure provides a hydrocarbon oil catalytic conversion method, comprising bringing a hydrocarbon oil into 20 contact with the hydrocarbon oil conversion catalyst according to the third aspect or the catalyst composition according to the fifth aspect for reaction.

Compared with the phosphorus-alumina sols of the prior art, the phosphorus-alumina sol provided by the present disclosure has a higher QP_0^2/QP_0^0 at the same P/Al ratio, indicating a higher degree of polymerization. 25 In addition to the higher degree of polymerization, the phosphorus-alumina sol provided by the present disclosure also has an appropriate colloidal particle size and a narrow size distribution, as well as high stability and good binding properties.

The phosphorus-alumina sol provided by the present disclosure can 30 undergo polymerization at high temperatures to form substances with high melting points and high binding properties, improving the strength, high-temperature resistance, and/or wear resistance of materials. The phosphorus-

alumina sol can be used as a binder for preparing catalysts, a binder for refractory materials, or an additive for coatings. For example, due to its appropriate colloidal particle size and higher degree of polymerization, when used in preparing a molecular sieve-containing catalyst such as a FCC catalyst, the phosphorus-alumina sol provided by the present disclosure can reduce blockage of molecular sieve pores and channels, improve the hydrothermal stability, catalytic performance, and mechanical strength of the catalyst, e.g., improve the wear resistance (attrition strength) and increase cracking activity, reactant conversion, and/or target product selectivity of the FCC catalyst, e.g., in some cases improve selectivity for gasoline, propylene, and/or butylene.

The phosphorus-alumina sol, the preparation method thereof, and the use thereof as a binder in a hydrocarbon oil conversion catalyst provided by the present disclosure have at least one of the following advantages, and under preferred conditions, have a plurality of or all of the following advantages:

1. The raw materials for preparing the phosphorus-alumina sol are low-cost aluminum salts and phosphates, thereby reducing production costs.

2. The synthesis period is shortened by adopting a specific preparation method.

3. By adopting specific raw materials for preparation and screening preparation procedures and reaction conditions, the stability of the phosphorus-alumina sol is improved, avoiding precipitation, solidification, or stratification, thereby extending the storage time and service life of the phosphorus-alumina sol.

4. The obtained phosphorus-alumina sol has a higher QP_0^2/QP_0^0 at the same P/Al ratio, indicating relatively fewer free phosphate, and relatively more polyphosphate, which can reduce the reaction of the phosphorus-alumina sol with other binders and simultaneously reduce the damaging effect on the extra-framework Al and framework Al of the molecular sieve, facilitating improvement of the activity and hydrothermal stability of the molecular sieve.

5. The obtained phosphorus-alumina sol has an appropriate and uniform colloidal particle size, abundant surface hydroxyl groups, as well as a higher degree of aggregation, and higher matrix activity, making it more compatible

with the molecular sieve, reducing blockage of molecular sieve pores and channels, and improving selectivity for light olefins of FCC catalysts.

6. The obtained phosphorus-alumina sol has good binding properties, and when used in catalyst preparation, can improve the mechanical strength of the catalyst.

7. The obtained phosphorus-alumina sol has a synergistic effect with the molecular sieve and other matrix materials in the catalyst, effectively increasing the yield of light olefins, increasing the olefin content in LPG, promoting heavy oil conversion, reducing coke and slurry oil, and/or increasing the yields of gasoline and LPG.

Additional features and advantages of the present application will be described in detail in the subsequent detailed description section.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings are intended to provide a further understanding of the present application, constitute a part of the specification, and together with the following detailed description serve to explain the present application, but do not constitute a limitation on the present application. In the accompanying drawings:

Figure 1 shows ^{31}P NMR spectra of the phosphorus-alumina sols obtained in Example 1 and Comparative Example 1.

Figure 2 shows a transmission electron microscopy image of the phosphorus-alumina sol obtained in Example 1.

DETAILED DESCRIPTION

The specific embodiments of the present application will be described in detail below with reference to the accompanying drawings. It should be understood that the specific embodiments described herein are only used to illustrate and explain the present application and are not intended to limit the present application.

Any specific numerical value (including the endpoints of numerical ranges) disclosed herein is not limited to the precise value of this numerical

value, but should be understood to also encompass values close to that precise value, such as all possible values within a range of $\pm 5\%$ of that precise value. Furthermore, for disclosed numerical ranges, one or more new numerical ranges can be obtained by arbitrary combination between the endpoint values of the range, between endpoint values and specific point values within the range, and between various specific point values. These new numerical ranges should also be considered as specifically disclosed herein.

Unless otherwise indicated, the terms used herein have the same meanings as commonly understood by a person skilled in the art. If a term is defined herein and the definition differs from the common understanding in the art, the definition herein shall prevail.

In the present application, the term "weakly acidic organic acid" refers to an organic compound that can only partially ionize hydrogen ions in an aqueous solution, thus exhibiting weak acidity, e.g., an organic acid having one or more, preferably 1-3, carboxyl (-COOH) functional groups.

In the present application, besides the explicitly described contents, any matters or items not mentioned are directly applicable to those known in the art without any modification. Moreover, any embodiment described herein can be freely combined with one or more other embodiments described herein, and the resulting technical solution or technical idea shall be regarded as originally disclosed or originally recorded in the present application, and shall not be considered as a new content not previously disclosed or anticipated, unless such combination is obviously unreasonable to a person skilled in the art.

All patents and non-patent documents mentioned herein, including but not limited to textbooks and journal articles, are incorporated by reference in their entirety.

Phosphorus-alumina sol

As described above, in the first aspect, the present disclosure provides a phosphorus-alumina sol, the phosphorus-alumina sol comprising Al, P, and a stabilizer, and having a P/Al weight ratio of 1.6-6 : 1, wherein $QP_0^2/QP_0^0 = 1.5-5$, and the phosphorus-alumina sol has an average colloidal particle size of

10-30 nm.

The P/Al weight ratio (on elemental basis) of the phosphorus-alumina sol according to the present disclosure is in a range of 1.6-6 : 1, e.g., 1.6-5.8 : 1, e.g., 1.7-5.6 : 1. In some embodiments, the P/Al weight ratio (on elemental basis) of the phosphorus-alumina sol may be 1.6 : 1, 1.7 : 1, 1.8 : 1, 1.9 : 1, 2 : 1, 2.1 : 1, 2.2 : 1, 2.3 : 1, 2.4 : 1, 2.5 : 1, 2.6 : 1, 2.7 : 1, 2.8 : 1, 2.9 : 1, 3 : 1, 3.1 : 1, 3.2 : 1, 3.3 : 1, 3.4 : 1, 3.5 : 1, 3.6 : 1, 3.7 : 1, 3.8 : 1, 3.9 : 1, 4 : 1, 4.1 : 1, 4.2 : 1, 4.3 : 1, 4.4 : 1, 4.5 : 1, 4.6 : 1, 4.7 : 1, 4.8 : 1, 4.9 : 1, 5 : 1, 5.1 : 1, 5.2 : 1, 5.3 : 1, 5.4 : 1, 5.5 : 1, 5.6 : 1, 5.7 : 1, 5.8 : 1, 5.9 : 1, 6 : 1, or within a range formed by any two of the above values.

The QP_0^2/QP_0^0 of the phosphorus-alumina sol according to the present disclosure is in a range of 1.5-5, e.g., 1.5-4, e.g., 1.5-3.3. In some embodiments, the QP_0^2/QP_0^0 of the phosphorus-alumina sol may be 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 5, or within a range formed by any two of the above values. In the ^{31}P NMR spectrum of the phosphorus-alumina sol, the resonance signal peak area at a chemical shift of -12 ± 2 ppm is defined as QP_0^2 , and the resonance signal peak area at a chemical shift of 0 ± 2 ppm is defined as QP_0^0 . At the same P/Al ratio, a higher QP_0^2/QP_0^0 indicates a higher degree of polymerization. A higher degree of polymerization means relatively fewer free phosphate and relatively more high-polymer-state phosphate, which can reduce the reaction of free phosphate in the phosphorus-alumina sol with other binders and simultaneously reduce the damaging effect on the extra-framework Al and framework Al of the molecular sieve, facilitating improvement of the activity and hydrothermal stability of the molecular sieve.

Preferably, the phosphorus-alumina sol according to the present disclosure may comprise Al in an amount, calculated as Al_2O_3 , of 3-15 wt%, e.g., 3-12 wt%. In some embodiments, the phosphorus-alumina sol may comprise Al in an amount, calculated as Al_2O_3 , of 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, 10 wt%, 11 wt%, 12 wt%, 13 wt%, 14 wt%, 15 wt%, or within a range formed by any two of the above values.

Preferably, the phosphorus-alumina sol according to the present disclosure may comprise P in an amount, calculated as P_2O_5 , of 15-40 wt%, e.g., 15-35 wt%. In some embodiments, the phosphorus-alumina sol may comprise P in an amount, calculated as P_2O_5 , of 15 wt%, 16 wt%, 17 wt%, 18 wt%, 19 wt%, 20 wt%, 21 wt%, 22 wt%, 23 wt%, 24 wt%, 25 wt%, 26 wt%, 27 wt%, 28 wt%, 29 wt%, 30 wt%, 31 wt%, 32 wt%, 33 wt%, 34 wt%, 35 wt%, 36 wt%, 37 wt%, 38 wt%, 39 wt%, 40 wt%, or within a range formed by any two of the above values.

Preferably, the phosphorus-alumina sol according to the present disclosure may comprise a stabilizer in an amount of 0.1-10 wt%, e.g., 0.5-5 wt%, or 2-4 wt%. In some embodiments, the phosphorus-alumina sol may comprise a stabilizer in an amount of 0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt%, 0.6 wt%, 0.7 wt%, 0.8 wt%, 0.9 wt%, 1.0 wt%, 1.5 wt%, 2 wt%, 2.5 wt%, 3 wt%, 3.5 wt%, 4 wt%, 4.5 wt%, 5 wt%, 5.5 wt%, 6 wt%, 6.5 wt%, 7 wt%, 7.5 wt%, 8 wt%, 8.5 wt%, 9 wt%, 9.5 wt%, 10 wt%, or within a range formed by any two of the above values.

Preferably, the stabilizer may be a weakly acidic organic acid. For example, the stabilizer may be selected from at least one of glycolic acid, oxalic acid, acetic acid, malonic acid, malic acid, tartaric acid, succinic acid, adipic acid, maleic acid, itaconic acid, and citric acid. The stabilizer is preferably oxalic acid, acetic acid, citric acid, or a combination thereof.

Preferably, the pH value of the phosphorus-alumina sol according to the present disclosure may be in a range of 0.5-2.5, e.g., 0.8-1.9. In some embodiments, the pH value of the phosphorus-alumina sol may be 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, or within a range formed by any two of the above values.

Preferably, the solid content of the phosphorus-alumina sol according to the present disclosure may be in a range of 15-50 wt%, preferably 20 wt%-45 wt%. In some embodiments, the solid content of the phosphorus-alumina sol may be 15 wt%, 16 wt%, 17 wt%, 18 wt%, 19 wt%, 20 wt%, 21 wt%, 22 wt%, 23 wt%, 24 wt%, 25 wt%, 26 wt%, 27 wt%, 28 wt%, 29 wt%, 30 wt%, 31 wt%, 32 wt%, 33 wt%, 34 wt%, 35 wt%, 36 wt%, 37 wt%, 38 wt%, 39 wt%, 40 wt%,

41 wt%, 42 wt%, 43 wt%, 44 wt%, 45 wt%, 46 wt%, 47 wt%, 48 wt%, 49 wt%, 50 wt%, or within a range formed by any two of the above values.

Preferably, the dynamic viscosity of the phosphorus-alumina sol according to the present disclosure may be in a range of 10-50 cP. In some embodiments, the dynamic viscosity of the phosphorus-alumina sol may be 10 cP, 11 cP, 12 cP, 13 cP, 14 cP, 15 cP, 16 cP, 17 cP, 18 cP, 19 cP, 20 cP, 21 cP, 22 cP, 23 cP, 24 cP, 25 cP, 26 cP, 27 cP, 28 cP, 29 cP, 30 cP, 31 cP, 32 cP, 33 cP, 34 cP, 35 cP, 36 cP, 37 cP, 38 cP, 39 cP, 40 cP, 41 cP, 42 cP, 43 cP, 44 cP, 45 cP, 46 cP, 47 cP, 48 cP, 49 cP, 50 cP, or within a range formed by any two of the above values.

The average colloidal particle size (also referred to as colloidal particle diameter) of the phosphorus-alumina sol according to the present disclosure is in a range of 10-30 nm, e.g., 15-28 nm. Preferably, the colloidal particle size of the phosphorus-alumina sol according to the present disclosure is mainly concentrated in a range of 10-30 nm, with an aggregation degree of colloidal particle size greater than 85%, e.g., 85-95%. That the colloidal particle size of the phosphorus-alumina sol is mainly concentrated in a range of 10-30 nm means that the aggregation degree of colloidal particles of the phosphorus-alumina sol having a colloidal particle size in the range of 10-30 nm is >85%. The aggregation degree refers to the ratio of the number of colloidal particles with a colloidal particle size in the range of 10-30 nm to the total number of colloidal particles. The colloidal particle size (also referred to as colloidal particle diameter) is measured by transmission electron microscopy and is the maximum projected dimension of the colloidal particle, and the average colloidal particle size is the arithmetic mean of the colloidal particle sizes. The phosphorus-alumina sol according to the present disclosure has an appropriate and uniform colloidal particle size, making it more compatible with the molecular sieve, reducing blockage of molecular sieve pores and channels, and improving the selectivity of the catalyst.

The phosphorus-alumina sol according to the present disclosure comprises a balance of water, preferably the water content is in a range of 10-30 wt%.

The phosphorus-alumina sol according to the present disclosure comprises cations derived from the phosphate, such as ammonium ions. The content of the cations derived from the phosphate is, for example, in a range of 5-15 wt%.

5 The phosphorus-alumina sol according to the present disclosure comprises inorganic acid radicals derived from the aluminum salt source, such as one or more of sulfate, chloride, and nitrate radicals. The content of the inorganic acid radicals is, for example, in a range of 10-50 wt%.

Preferably, the molar ratio of organic acid radicals of the stabilizer to Al
10 in the phosphorus-alumina sol according to the present disclosure is in a range of 0.05-0.5 : 1. In some embodiments, the molar ratio of organic acid radicals of the stabilizer to Al in the phosphorus-alumina sol may be 0.05 : 1, 0.06 : 1, 0.07 : 1, 0.08 : 1, 0.09 : 1, 0.1 : 1, 0.15 : 1, 0.2 : 1, 0.25 : 1, 0.3 : 1, 0.35 : 1, 0.4 : 1, 0.45 : 1, 0.5 : 1, or within a range formed by any two of the above
15 values.

Compared with the phosphorus-alumina sols of the prior art, the phosphorus-alumina sol according to the present disclosure has a higher degree of polymerization at the same P/Al ratio. In addition, the phosphorus-alumina sol according to the present disclosure also has an appropriate colloidal particle
20 size and a narrow size distribution, as well as high stability and good binding properties. The phosphorus-alumina sol according to the present disclosure can undergo polymerization at high temperatures to form substances with high melting points and high binding properties, improving the strength, high-temperature resistance, and/or wear resistance of materials. The phosphorus-
25 alumina sol can be used as a binder for preparing catalysts, a binder for refractory materials, or an additive for coatings. For example, due to its appropriate colloidal particle size and higher degree of polymerization, when used in preparing a molecular sieve-containing catalyst such as a FCC catalyst, the phosphorus-alumina sol according to the present disclosure can reduce
30 blockage of molecular sieve pores and channels, improve the hydrothermal stability, catalytic performance, and mechanical strength of the catalyst, e.g., improve the wear resistance (attrition strength) and increase cracking activity,

reactant conversion, and/or target product selectivity of the FCC catalyst, e.g., in some cases improve selectivity for gasoline, propylene, and/or butylene.

Preparation Method of Phosphorus-alumina sol

5 In a second aspect, the present disclosure also provides a method for preparing the phosphorus-alumina sol according to the first aspect, comprising:

1) under stirring at a temperature of 50°C-95°C, mixing an aluminum salt source, decationized water, and a stabilizer to form a slurry, so as to obtain an alumina precursor solution.

10 2) under stirring at a temperature of 25°C-70°C, adding a phosphate to the alumina precursor solution at a P/Al weight ratio of 1.6-6 : 1 for reaction, so as to obtain a phosphorus-alumina sol.

Preferably, the temperature in step 1) is in a range of 60°C-90°C; the temperature in step 2) is in a range of 30-55°C.

15 Preferably, the aluminum salt source may be one or more of aluminum nitrate, aluminum sulfate, and aluminum chloride.

Preferably, the phosphate may be diammonium hydrogen phosphate and/or ammonium dihydrogen phosphate. The phosphate may be added by adding a phosphate solution or by adding a phosphate solid.

20 Preferably, the stabilizer may be a weakly acidic organic acid, for example, the stabilizer may be selected from at least one of glycolic acid, oxalic acid, acetic acid, malonic acid, malic acid, tartaric acid, succinic acid, adipic acid, maleic acid, itaconic acid, and citric acid. The stabilizer is preferably oxalic acid, acetic acid, citric acid, or a combination thereof.

25 In step 1), the decationized water (also referred to as cation-removed water or acidic water) is well known to a person skilled in the art. The pH value of the decationized water is preferably in a range of 2.8-3.2, and the sodium oxide content is preferably <5 ppm.

30 Preferably, in step 1), the weight ratio of the aluminum salt source, decationized water, and stabilizer is in a range of 100 : (50-800) : (5-40), preferably 100 : (100-750) : (6-35), with the aluminum salt source calculated as aluminum oxide;

In step 2), the weight ratio of the alumina precursor solution to the phosphate is in a range of 100 : (50-200), preferably 100 : (60-150), with the phosphate calculated as phosphorus oxide.

Preferably, the pH value of the alumina precursor solution may be in a range of 0.5-3.0, e.g., 0.6-2, e.g., 0.7-1.5. In some embodiments, the pH value of the alumina precursor solution may be 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, or within a range formed by any two of the above values.

Preferably, the solid content of the alumina precursor solution may be in a range of 5-40 wt%. In some embodiments, the solid content of the alumina precursor solution may be 5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, 10 wt%, 11 wt%, 12 wt%, 13 wt%, 14 wt%, 15 wt%, 16 wt%, 17 wt%, 18 wt%, 19 wt%, 20 wt%, 21 wt%, 22 wt%, 23 wt%, 24 wt%, 25 wt%, 26 wt%, 27 wt%, 28 wt%, 29 wt%, 30 wt%, 31 wt%, 32 wt%, 33 wt%, 34 wt%, 35 wt%, 36 wt%, 37 wt%, 38 wt%, 39 wt%, 40 wt%, or within a range formed by any two of the above values.

Preferably, in step 1), the slurry mixing time is 5 minutes or more, e.g., 10-50 minutes; in step 2), the reaction time is in a range of 10-60 minutes.

Preferably, the temperature in step 2) may be lower than the temperature in step 1) by 10-50°C, e.g., lower by 10°C, 15°C, 20°C, 25°C, 30°C, 35°C, 40°C, 45°C, 50°C, or within a range formed by any two of the above values. In some embodiments, step 2) may be carried out under heat preservation or temperature control conditions. In other embodiments, step 2) may be carried out under non-heating, slow cooling conditions.

Preferably, the method for preparing the phosphorus-alumina sol may comprise:

1) under stirring at a temperature of 50°C-95°C, e.g., 60-80°C, mixing an aluminum salt source, deionized water, and a stabilizer to form a slurry, so as to obtain an alumina precursor solution with a solid content of 5-40 wt%, for a slurry mixing time of 10-50 minutes, to hydrolyze the aluminum salt source, then stopping heating;

2) under stirring at a temperature of 25°C-70°C, e.g., 35-55°C, adding a

phosphate to the above alumina precursor solution at a P/Al weight ratio of 1.6-6 : 1, and slowly reacting for 10-60 minutes until a transparent colloid is formed.

By adopting the specific preparation method according to the present disclosure, the synthesis time of the phosphorus-alumina sol is shortened, the preparation cost of the phosphorus-alumina sol is reduced, and the stability of the phosphorus-alumina sol is improved, avoiding precipitation, solidification, or stratification, thereby extending the storage time and service life of the phosphorus-alumina sol, making it possible to obtain a phosphorus-alumina sol having an appropriate colloidal particle size, a high degree of polymerization, high stability, and good binding properties.

Hydrocarbon Oil Conversion Catalyst

In a third aspect, the present disclosure also provides a hydrocarbon oil conversion catalyst, the catalyst comprising a molecular sieve, a phosphorus-alumina binder, other inorganic binder(s) different from the phosphorus-alumina binder, an optional metal component, an optional meso-macroporous inorganic oxide material, and an optional clay, wherein the phosphorus-alumina binder is the phosphorus-alumina sol according to the first aspect or the phosphorus-alumina sol prepared by the method according to the second aspect, or is derived from the phosphorus-alumina sol according to the first aspect or the phosphorus-alumina sol prepared by the method according to the second aspect.

Preferably, the molecular sieve may be selected from an MFI molecular sieve, a BEA molecular sieve, or a combination thereof.

According to the present disclosure, the other inorganic binder(s) may be those conventionally used by a person skilled in the art in preparing catalysts. Preferably, the other inorganic binder(s) may be selected from one or more of pseudo-boehmite, acidified pseudo-boehmite, alumina sol, silica-alumina sol, and silica sol.

According to the present disclosure, the clay may be those conventionally used by a person skilled in the art in preparing catalysts. Preferably, the clay

may be selected from one or more of kaolin, sepiolite, attapulgite, rectorite, montmorillonite, and diatomite.

First Embodiment of the Third Aspect

In a first embodiment of the third aspect, the catalyst comprises a
5 molecular sieve, a phosphorus-alumina binder, other inorganic binder(s), a metal component, and an optional clay.

Preferably, based on the dry weight of the catalyst, the molecular sieve is present in an amount of 25-75 wt%, the metal component is present in an amount, calculated as metal oxide, of 0.5-8 wt%, the phosphorus-alumina
10 binder is present in an amount, calculated as oxide, of 3-40 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 1-25 wt%, and the clay is present in an amount of 0-30 wt%.

More preferably, based on the dry weight of the catalyst, the molecular sieve is present in an amount of 30-65 wt%, the metal component is present in
15 an amount, calculated as metal oxide, of 0.8-6 wt%, the phosphorus-alumina binder is present in an amount, calculated as oxide, of 8-32 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 2-20 wt%, and the clay is present in an amount of 1-25 wt%.

Further preferably, based on the dry weight of the catalyst, the molecular
20 sieve is present in an amount of 40-60 wt%, the metal component is present in an amount, calculated as metal oxide, of 1-5.5 wt%, the phosphorus-alumina binder is present in an amount, calculated as oxide, of 20-30 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 10-18 wt%, and the clay is present in an amount of 5-10 wt%.

25 The catalyst having the above composition exhibits better catalytic performance, can further increase the yield of light olefins, promote the conversion of heavy oil, and/or reduce coke and slurry oil.

Preferably, the catalyst has a pore volume determined by BJH method of greater than 0.12 mL/g, e.g., 0.12-0.14 mL/g, more preferably greater than
30 0.122 mL/g.

Preferably, the metal in the metal component is selected from at least one of Group VIII metals, preferably one or more of Fe, Co, and Ni.

Preferably, the molecular sieve comprises an MFI molecular sieve and a BEA molecular sieve, the molecular sieve comprises a first phosphorus component, the phosphorus-alumina binder comprises a second phosphorus component, and the first phosphorus component and the second phosphorus component are present in the catalyst in a total amount, calculated as P_2O_5 , of 10-35 wt%, e.g., 15-25 wt%.

Preferably, the MFI molecular sieve and the BEA molecular sieve are each independently selected from one or more of a hydrogen-form molecular sieve, a phosphorus-containing molecular sieve, and a phosphorus- and transition metal-containing molecular sieve. In a preferable embodiment, at least one of the MFI molecular sieve and the BEA molecular sieve comprises phosphorus; preferably, the MFI molecular sieve and the BEA molecular sieve are each independently a phosphorus- and transition metal-containing molecular sieve, i.e., the MFI molecular sieve may comprise both phosphorus and a transition metal, and the BEA molecular sieve may comprise both phosphorus and a transition metal. The MFI molecular sieve and/or the BEA molecular sieve may comprise a modifying metal, wherein the modifying metal contained therein is not counted as part of the metal component but is considered as part of the molecular sieve component. Preferably, the modifying metal in the molecular sieve and the metal component are present in a total amount of 0.5-8 wt%.

Preferably, the MFI molecular sieve is a multi-level porous ZSM-5 molecular sieve having a silica-alumina ratio of 20-70, a pore volume determined by BJH method of greater than 0.25 mL/g, a pore volume of pores with a pore size of 2-50 nm accounting for 40-70% of the total pore volume; a pore volume of pores with a pore size of 2-20 nm accounting for 85% or more of the total mesopore volume, and a micropore volume of greater than 0.1 cc/g.

Preferably, the BEA molecular sieve is a β molecular sieve having a micropore specific surface area of 450-500 m^2/g , wherein the mesopore volume of the β molecular sieve accounts for 35-60 vol% of the total pore volume; the strong acid amount of the molecular sieve accounts for 25-55% of the total acid amount, and the ratio of B acid amount to L acid amount is in a

range of 35-75.

According to the present disclosure, the pore volume determined by BJH method, total pore volume, and micropore volume are measured according to the RIPP 151-90 method (see Petrochemical Analytical Methods, Nitrogen Adsorption Capacity Method for Determining Pore Volume and Pore Size Distribution of Catalysts, "Petrochemical Analytical Methods" (RIPP Test Methods), edited by Yang Cuiding et al., Science Press, 1990).

Preferably, the weight ratio of the BEA molecular sieve to the MFI molecular sieve is in a range of (0.01-100):1, preferably (0.1-30):1, further preferably (0.25-6):1. When the BEA molecular sieve and the MFI molecular sieve in the above ratio are used as the molecular sieve, it is possible to further increase the catalyst performance towards the content of propylene and butylene in liquefied gas, increase the olefin content in LPG, promote diesel cracking, and/or reduce gasoline loss, thereby reducing the yields of diesel and slurry oil and increasing the yields of gasoline and LPG.

Second Embodiment of the Third Aspect

In a second embodiment of the third aspect, the catalyst comprises a molecular sieve, a phosphorus-alumina binder, other inorganic binder(s), a meso-macroporous inorganic oxide material, and an optional clay, wherein the meso-macroporous inorganic oxide material is preferably a macroporous alumina material, and the molecular sieve is preferably an MFI molecular sieve.

Preferably, based on the dry weight of the catalyst, the MFI molecular sieve is present in an amount of 10-75 wt%, the macroporous alumina material is present in an amount of 1-30 wt%, the phosphorus-alumina binder is present in an amount, calculated as oxide, of 3-35 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 1-20 wt%, and the clay is present in an amount of 0-60 wt%.

More preferably, based on the dry weight of the catalyst, the MFI molecular sieve is present in an amount of 15-65 wt%, the macroporous alumina material is present in an amount of 2-25 wt%, the phosphorus-alumina binder is present in an amount, calculated as oxide, of 8-32 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 2-20 wt%,

and the clay is present in an amount of 1-25 wt%.

Further preferably, based on the dry weight of the catalyst, the MFI molecular sieve is present in an amount of 20-60 wt%, the macroporous alumina material is present in an amount of 2-20 wt%, the phosphorus-alumina binder is present in an amount, calculated as oxide, of 20-30 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 10-18 wt%, and the clay is present in an amount of 5-10 wt%.

The catalyst having the above composition exhibits better catalytic performance, can further increase the yield of light olefins, promote the conversion of heavy oil, and reduce coke and slurry oil.

Preferably, the MFI molecular sieve is selected from one or more of a hydrogen-form MFI molecular sieve, a phosphorus-containing MFI molecular sieve, and a transition metal-containing MFI molecular sieve.

Preferably, the macroporous alumina material has a bimodal pore distribution structure, with the pore volume of pores having a pore size of 2-10 nm accounting for 20-40% of the total pore volume, and the pore volume of pores having a pore size of 10-100 nm accounting for 60-80% of the total pore volume. The macroporous alumina material having a bimodal structure means that the pore distribution spectrum measured by the nitrogen adsorption capacity method for the macroporous alumina material exhibits two distinct spectral peaks.

The macroporous alumina material having a bimodal macroporous distribution is conducive to the diffusion of heavy oil macromolecules and reactant molecules, promotes pre-cracking of heavy oil, and reduces coke formation. The phosphorus-alumina binder, the macroporous alumina material, and the MFI molecular sieve have a synergistic effect, effectively increasing the yield of light olefins (e.g., propylene) and the content of light olefins (e.g., propylene) in liquefied gas, promoting heavy oil conversion, and/or reducing coke and slurry oil.

Third Embodiment of the Third Aspect

In a third embodiment of the third aspect, the catalyst comprises a molecular sieve, a phosphorus-alumina binder, other inorganic binder(s), a

meso-macroporous inorganic oxide material, and an optional clay, wherein the meso-macroporous inorganic oxide material is preferably a porous silica-alumina composite material, and the molecular sieve is preferably an MFI molecular sieve.

5 Preferably, based on the dry weight of the catalyst, the MFI molecular sieve is present in an amount of 10-75 wt%, the porous silica-alumina composite material is present in an amount of 1-30 wt%, the phosphorus-alumina binder is present in an amount, calculated as oxide, of 3-35 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 1-20
10 wt%, and the clay is present in an amount of 0-60 wt%.

More preferably, based on the dry weight of the catalyst, the MFI molecular sieve is present in an amount of 15-65 wt%, the porous silica-alumina composite material is present in an amount of 2-25 wt%, the phosphorus-alumina binder is present in an amount, calculated as oxide, of 8-
15 32 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 2-20 wt%, and the clay is present in an amount of 1-25 wt%.

Further preferably, based on the dry weight of the catalyst, the MFI molecular sieve is present in an amount of 20-60 wt%, the porous silica-alumina composite material is present in an amount of 2-20 wt%, the
20 phosphorus-alumina binder is present in an amount, calculated as oxide, of 10-30 wt%, the other inorganic binder(s) is present in an amount, calculated as oxide, of 10-18 wt%, and the clay is present in an amount of 5-10 wt%.

Preferably, the MFI molecular sieve is selected from one or more of a hydrogen-form MFI molecular sieve, a phosphorus-containing MFI molecular
25 sieve, and a transition metal-containing MFI molecular sieve.

Preferably, the porous silica-alumina composite material has a mass composition of $(0.01-1)\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : (2-5)\text{SiO}_2$, a specific surface area of 300-600 m^2/g , a total pore volume of 0.15-0.4 mL/g , and a pore volume of meso-macropores having a pore size of 2-50 nm accounting for 20-40% of the
30 total pore volume.

Preferably, the porous silica-alumina composite material is obtained by hydrothermal crystallization of kaolin. In a specific embodiment, the porous

silica-alumina composite material is prepared by a method comprising the following steps:

a) treating metakaolin obtained by calcining kaolin with an inorganic acid at a temperature of 80-95°C to obtain a first mixture;

5 b) mixing the first mixture, sodium silicate, a directing agent, and an alkali solution to obtain a second mixture; wherein the second mixture has a composition with a weight ratio of $(0.1-5)\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : (2-10)\text{SiO}_2 : (5-100)\text{H}_2\text{O}$;

10 c) subjecting the second mixture to hydrothermal crystallization treatment, then discharging, filtering, and washing the solid product to obtain the porous silica-alumina composite material.

Preferably, in step a), the weight ratio of the inorganic acid to the metakaolin is in a range of $(0.01-0.1) : 1$, wherein the inorganic acid is calculated as H^+ , and the metakaolin is calculated on a dry weight basis;

15 the weight ratio of the directing agent to the metakaolin is in a range of $(0.01-1.0) : 1$, and the directing agent is calculated on a dry weight basis of oxide.

Preferably, in step b), the alkali solution may be one or more of sodium hydroxide solution, ammonia water, potassium hydroxide, magnesium
20 hydroxide, and sodium carbonate.

The present disclosure does not specifically limit the means for discharging the solid in step c), for example, it may be suction filtration, centrifugal separation, filtration, etc. In a preferable specific embodiment, the solid product in step c) is discharged, then washed with water and dried.
25 According to the present disclosure, hydrothermal crystallization treatment is well known to a person skilled in the art. In a preferable specific embodiment, the conditions of the hydrothermal crystallization treatment include: a temperature of 90-98°C, a time of 4-32 h. The hydrothermal crystallization treatment may be carried out under the autogenous pressure of the system or
30 under externally applied pressure, preferably under the autogenous pressure of the system.

According to the present disclosure, in step a), kaolin is calcined at a

temperature of 700-900°C for a time of 1-3 h to obtain the metakaolin. In a specific embodiment, in step a), the weight ratio of the inorganic acid to the metakaolin is in a range of (0.01-0.1) : 1, wherein the inorganic acid is calculated as H⁺, and the metakaolin is calculated on a dry weight basis; the weight ratio of the directing agent to the metakaolin is in a range of (0.01-1.0) : 1, and the directing agent is calculated on a dry weight basis of oxide. According to the present disclosure, the inorganic acid may include but is not limited to hydrochloric acid, sulfuric acid, nitric acid, etc. The directing agent is well known to a person skilled in the art, such as a directing agent for synthesis of NaY molecular sieve. In a specific embodiment, the directing agent has a molar composition of (10-17)SiO₂ : (0.7-1.3)Al₂O₃ : (11-18)Na₂O : (200-350)H₂O. The directing agent may be synthesized according to conventional methods, such as the preparation methods in USP3574538, USP3639099, USP3671191, USP4166099, and EUP0435625.

The porous silica-alumina composite material, on the one hand, has abundant mesopores to improve the diffusion of raw material molecules and reactants, and on the other hand, can improve the activity of the matrix, facilitating the cracking of heavy oil molecules and increasing gasoline olefins as propylene precursors. The phosphorus-alumina binder, the porous silica-alumina composite material, and the MFI molecular sieve have a synergistic effect, enabling the catalyst to increase the yields of catalytic cracking liquefied gas and propylene, with high total yields of gasoline and liquefied gas, lower coke yield, higher total liquid yield and conversion, significantly improving heavy oil cracking ability and propylene selectivity.

Method for Preparing Hydrocarbon Oil Conversion Catalyst

In a fourth aspect, the present disclosure also provides a method for preparing the hydrocarbon oil conversion catalyst according to the third aspect, the method comprising:

a) mixing the molecular sieve, the other inorganic binder(s), a metal source of the optional metal component, the optional meso-macroporous inorganic oxide material, the optional clay, and water to form a slurry,

controlling pH value of the slurry to be greater than 2.5, so as to obtain a first slurry;

b) mixing the first slurry with the phosphorus-alumina binder to obtain a second slurry, followed by spray drying and calcination, so as to obtain the catalyst.

Preferably, in step a), the molecular sieve, the optional meso-macroporous inorganic oxide material, the optional clay, and water are first mixed to form a slurry, and then the other inorganic binder(s) is added to the obtained mixture and mixed to form a slurry, so as to obtain the first slurry. This is beneficial for further improving the catalytic performance and mechanical strength of the catalyst.

Preferably, in step a), pH value of the slurry is controlled to be greater than 2.5, preferably greater than 2.5 and less than 5. In some embodiments, pH value of the slurry is controlled to be 2.6, 2.7, 2.8, 2.9, 3, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, or within a range formed by any two of the above values.

Preferably, the metal source is one or more of an iron salt, a cobalt salt, and a nickel salt, preferably $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

According to the present disclosure, spray drying is a technical means well known to a person skilled in the art, and the specific method will not be described in detail herein. Preferably, the spray drying may be conducted at an inlet temperature of 300-700°C, and an outlet temperature of 80-200°C.

Preferably, the calcination is conducted at a temperature of 400-700°C, preferably 450-600°C, for a time of 0.5-100 hours, preferably 0.5-10 hours.

Catalyst Composition and Use Thereof

In a fifth aspect, the present disclosure provides a catalyst composition, the catalyst composition comprising a cocatalyst and an optional procatalyst, wherein the cocatalyst is the hydrocarbon oil conversion catalyst according to the third aspect.

According to the present disclosure, the procatalyst may be those conventionally used by a person skilled in the art in hydrocarbon oil catalytic

conversion processes. Preferably, the procatalyst is a catalytic cracking catalyst.

Preferably, the weight ratio of the procatalyst to the cocatalyst is in a range of 100:15-100:2. In some embodiments, the weight ratio of the procatalyst to the cocatalyst may be 100:15, 100:14, 100:13, 100:12, 100:11, 100:10, 100:9, 100:8, 100:7, 100:6, 100:5, 100:4, 100:3, 100:2, or within a range formed by any two of the above values.

The present disclosure also provides use of the hydrocarbon oil conversion catalyst according to the third aspect or the catalyst composition according to the fifth aspect in a hydrocarbon oil catalytic conversion reaction.

In a sixth aspect, the present disclosure provides a hydrocarbon oil catalytic conversion method, comprising bringing a hydrocarbon oil into contact with the hydrocarbon oil conversion catalyst according to the third aspect or the catalyst composition according to the fifth aspect for reaction.

Preferably, the reaction is conducted under conditions including: a temperature of 300-700°C, preferably 400-600°C, more preferably 400-550°C; and/or a weight hourly space velocity of 4-120 h⁻¹, preferably 4-80 h⁻¹, more preferably 8-16 h⁻¹; and/or a catalyst-to-oil ratio by weight of 1-20, preferably 2-10, more preferably 4-8.

According to the present disclosure, the hydrocarbon oil may include but is not limited to wax oil, residual oil, and recycle oil.

The hydrocarbon oil catalytic conversion method according to the present disclosure may be carried out using various existing catalytic cracking reactors, such as fixed bed reactors, fluidized bed reactors, riser reactors, multi-reaction zone reactors, etc.

The hydrocarbon oil catalytic conversion method provided by the present disclosure, by using the catalyst or catalyst composition according to the present disclosure having improved hydrothermal stability, catalytic performance, and mechanical strength, can increase reactant conversion and target product selectivity, e.g., in some cases improve gasoline, propylene, and/or butylene selectivity, promote heavy oil conversion, and reduce coke and slurry oil.

To facilitate understanding of the present disclosure, the present disclosure provides examples as follows. However, these examples are only for helping to understand the present disclosure and should not be considered as specific limitations on the present disclosure.

5

EXAMPLES

The present disclosure is further described below by means of specific examples, but this does not constitute a limitation on the present disclosure.

10 In the following examples and comparative examples, the raw materials used were as follows:

Pseudo-boehmite: CHALCO Shandong Co., Ltd., solid content: 60 wt%;

Concentrated phosphoric acid: Beijing Chemical Works, chemically pure, 85 wt%;

15 Decationized water (acidic water): pH 2.8-3.2, sodium oxide content <5 ppm (mass);

Kaolin: catalyst-specific kaolin produced by China Kaolin Co., Ltd., quartz sand <3.5 wt%, Al_2O_3 44.0 wt%, Fe_2O_3 0.56 wt%, Na_2O 1.5 wt%, solid content: 80 wt%;

20 Anhydrous aluminum sulfate: China National Pharmaceutical Group Co., Ltd., analytically pure, content: 99%;

Aluminum nitrate nonahydrate: China National Pharmaceutical Group Co., Ltd., analytically pure, content: 99%;

Ammonium dihydrogen phosphate: China National Pharmaceutical Group Co., Ltd., analytically pure, content: 99%;

25 Diammonium hydrogen phosphate: China National Pharmaceutical Group Co., Ltd., analytically pure, content: 99%;

Oxalic acid: China National Pharmaceutical Group Co., Ltd., analytically pure, 99% purity;

30 Hydrochloric acid: China National Pharmaceutical Group Co., Ltd./Beijing Chemical Works, analytically pure, concentration: 36-38 wt%;

Alumina sol: Sinopec Catalyst Qilu Branch, Al_2O_3 content: 21.5 wt%;

Kaolin: China Kaolin Co., Ltd. (Suzhou), solid content: 78 wt%;

FeCl₃·6H₂O: Xilong Scientific Co., Ltd., chemically pure, purity: 99%;

MPZ molecular sieve: Sinopec Catalyst Qilu Branch, P₂O₅ content: 7.25 wt%, Fe₂O₃ content: 1.95 wt%, crystallinity: 72%;

5 Phosphorus-containing β molecular sieve: H-β molecular sieve was impregnated with a 0.2 mol/L ammonium dihydrogen phosphate solution by saturation impregnation, stirred for two hours, dried at 120°C for 10 hours, and calcined at 500°C for 3 hours to obtain a phosphorus-modified β molecular sieve P-β with a P₂O₅ content of 6.23 wt% and a crystallinity of 78%;

10 Macroporous alumina material: CHALCO Shandong Co., Ltd., solid content: 80 wt%, pore volume of pores with a pore size of 2-10 nm accounting for 20-40% of the total pore volume, pore volume of pores with a pore size of 10-100 nm accounting for 60-80% of the total pore volume;

Sodium silicate solution: SiO₂ 20.65 wt%, Na₂O 5.25 wt%, industrial grade;

15 Catalytic cracking catalyst SLA-1: Sinopec Catalyst Qilu Branch;

Catalytic cracking catalyst SLA-2: Sinopec Catalyst Qilu Branch.

In the following examples, unless otherwise stated, percentages and parts are by weight.

20 Test methods:

Matrix activity and micro-activity were measured according to Q/SH 3360 211-2007, matrix strength was measured according to Q/SH 3360 208-2006.

25 In the examples and comparative examples, ³¹P NMR was tested using a Bruker Avance III 500 MHz nuclear magnetic resonance spectrometer at a resonance frequency of 202.474 MHz, with H₃PO₄ as the calibration compound. The resonance peak spectra were subjected to peak fitting and then the peak areas were calculated using the integration method. Each chemical shift corresponds to a phosphorus chemical environment, designated as QP_mⁿ,
30 where m represents the number of Al-O-P and n represents the number of P-O-P, as follows:

0±2 ppm: QP₀⁰ represents one phosphorus-oxygen tetrahedron [PO₄] or

an orthophosphoric acid molecule;

-7±2 ppm: QP_0^1 represents that P is bonded to one phosphorus-oxygen-hydroxyl, P-O-P;

5 -12±2 ppm: QP_0^2 represents that P is bonded to two phosphorus-oxygen-hydroxyls, P-O-P-O-P;

-17±2 ppm: QP_1^1 represents one Al-O-P-O-P.

The colloidal particle size of the phosphorus-alumina sol was measured using an FEI Tecnai G2 F20 field emission transmission electron microscope (TEM) from FEI, USA. Test conditions: accelerating voltage of the instrument
10 200 kV, point resolution 0.24 nm.

100 colloidal particles of the phosphorus-alumina sol were randomly selected on the TEM image, and their maximum projected dimensions were measured as the colloidal particle size. The arithmetic mean was calculated as the average colloidal particle size. The proportion of the number of colloidal
15 particles with a colloidal particle size in a range of 10-30 nm to the total number of colloidal particles was the aggregation degree.

The component contents in the phosphorus-alumina sol were measured and calculated by inductively coupled plasma emission spectroscopy (ICP). The component contents in the catalyst, such as oxide contents, were measured
20 by X-ray fluorescence spectroscopy (see “Petrochemical Analytical Methods”, edited by Yang Cuiding et al., Science Press, 1990).

The dynamic viscosity of the phosphorus-alumina sol was measured using a SYD-265B petroleum product kinematic viscometer according to GB/T 265 “Petroleum products - Determination of kinematic viscosity and calculation of
25 dynamic viscosity”.

When the prepared catalysts were evaluated for catalytic cracking reaction performance, an ACE apparatus was used for evaluation.

The RIPP standard methods mentioned in the present disclosure can be found in “Petrochemical Analytical Methods” (RIPP Test Methods), edited by
30 Yang Cuiding et al., Science Press, 1990.

Nitrogen adsorption method (GB/T5816-1995) was used for determining specific surface area and pore volume: In the determination by nitrogen

adsorption method (RIPP 151-90, "Nitrogen Adsorption Capacity Method for Determining Pore Volume and Pore Size Distribution of Catalysts", see "Petrochemical Analytical Methods" (RIPP Test Methods), edited by Yang Cuiding et al., Science Press, 1990), pores larger than 2 nm are defined as meso-macropores, and the meso-macroporous ratio is calculated as $(V_{\text{total}} - V_{\text{micro}}) / V_{\text{total}} \times 100\%$.

Examples 1-4 and Comparative Examples 1-3 are preparation examples of phosphorus-alumina sols.

Example 1 of Phosphorus-alumina sol

0.56 kg of anhydrous aluminum sulfate was mixed with 0.25 kg of decaionized water and 0.05 kg of oxalic acid under stirring, and the temperature was raised to 70°C, followed by slurry mixing for 30 minutes. Then, the temperature was controlled at 45°C, and 0.56 Kg of ammonium dihydrogen phosphate was added to the slurry under stirring, followed by reaction at 45°C under stirring for 45 minutes to obtain a phosphorus-alumina sol P-1. The material proportions and product properties are shown in Table 1.

Figure 1 shows the ^{31}P NMR spectrum of the phosphorus-alumina sol obtained in this example. It can be seen from Figure 1 that at the same P/Al ratio, the product of Example 1 has a higher $\text{QP}_0^2/\text{QP}_0^0$ compared to the product of Comparative Example 1.

Figure 2 shows a transmission electron microscopy image of the phosphorus-alumina sol obtained in this example. It can be seen from Figure 2 that the colloidal particles of the phosphorus-alumina sol according to the present disclosure are in a monodisperse distribution.

Examples 2-4 of Phosphorus-alumina sol

Examples 2-4 followed the procedure of Example 1 but with different material proportions to prepare phosphorus-alumina sols. The material proportions and product properties are shown in Table 1.

Comparative Example 1 of Phosphorus-alumina sol

A phosphorus-alumina sol was prepared according to Chinese patent ZL201110180891.X.

At room temperature (25°C), 0.98 kg of pseudo-boehmite (containing 0.6 kg of Al₂O₃) and 0.2 kg of kaolin (dry basis 0.16 kg) were mixed with 0.44 kg of decaionized water, and the mixture was slurried for 30 minutes. Under stirring, 2.01 kg of concentrated phosphoric acid (85% by mass) was added to the slurry at an addition rate of 0.03 kg phosphoric acid/minute/Kg alumina source. The temperature was raised to 70°C, and then the mixture was reacted at this temperature for 45 minutes to obtain a phosphorus-alumina sol DP-1. The material proportions and product properties are shown in Table 1.

Comparative Example 2 of Phosphorus-alumina sol

(1) 0.27 kg of pseudo-boehmite (dry basis) was mixed with 0.24 kg of decaionized water at 20°C, stirred and slurried for 60 min to obtain a pseudo-boehmite slurry;

(2) 0.40 kg of phosphoric acid was dropped into the pseudo-boehmite slurry for a first contact, the temperature after the first contact was 23°C, followed by stirring for 30 min;

(3) 0.134 kg of phosphoric acid was dropped into the mixture after the first contact for a second contact to obtain a mixture with a temperature of 32°C, then the mixture was heated to 60°C under stirring, and stirred at 60°C for 90 min to obtain a phosphorus-alumina sol DP-2. The material proportions and product properties are shown in Table 1.

Comparative Example 3 of Phosphorus-alumina sol

Comparative Example 3 followed the procedure of Comparative Example 2 but with different material proportions to prepare a phosphorus-alumina sol. The material proportions and product properties are shown in Table 1.

Matrix Example 1

55 g (on dry basis) of the phosphorus-alumina sol of Example 1, 25 g (on dry basis) of acidified pseudo-boehmite (acid/pseudo-boehmite ratio (hydrochloric acid mass/pseudo-boehmite on dry basis) = 0.16, acidified pseudo-boehmite slurry with a solid content of 10 wt%), and 20 g (on dry basis) of kaolin were mixed and slurried with stirring for 15 min, spray-dried, and calcined at 500°C for 2 h.

Matrix Examples 2-4

Matrix Examples 2-4 followed the procedure of Matrix Example 1 but using the phosphorus-alumina sols of Examples 2-4, respectively.

Matrix Comparative Examples 1-3

Matrix Comparative Examples 1-3 followed the procedure of Matrix Example 1 but using the phosphorus-alumina sols of Comparative Examples 1-3, respectively.

The properties of the matrices prepared in Matrix Examples 1-4 and Comparative Examples 1-3 are shown in Table 1.

Table 1.

Example No.	Ex. 1	Ex. 2	Ex. 3	Ex. 4	CE. 1	CE. 2	CE. 3
Phosphorus-alumina sol	P-1	P-2	P-3	P-4	DP-1	DP-2	DP-3
Material amounts, Kg							
Aluminum sulfate	0.56						
Aluminum nitrate		1.03		0.49			
Aluminum chloride			0.31				
NH ₄ H ₂ PO ₄	0.56		0.64				
(NH ₄) ₂ HPO ₄		0.70		0.83			
Oxalic acid	0.05	0.03	0.05	0.05			
Pseudo-boehmite					0.98	0.27	0.11
Kaolin					0.2		
Phosphoric acid					2.01	0.534	0.71
Water	0.25	0.4	0.15	0.5	0.44	0.24	1.07
Solid content, wt%	39	25	45	27	55	50	27
Properties of Phosphorus-alumina sol							
Alumina content, wt%	11.51	6.26	10.06	3.46	16.53	15.78	3.45
Phosphorus oxide content, wt%	23.80	16.94	33.68	23.17	34.16	31.50	23.10

Stabilizer content, wt%	3.53	1.39	0.87	0.53	-	-	-
P/Al weight ratio	1.71	2.23	2.76	5.52	1.70	1.60	5.52
pH of alumina precursor solution	1.40	0.72	1.23	0.83	6.8	5.6	5.5
pH of phosphorus-alumina sol	1.86	0.81	1.75	0.95	2.46	2.1	0.78
QP_0^2/QP_0^0	3.24	1.85	1.61	1.52	0.92	1.29	1.12
Average colloidal particle size, nm	28	22	26	15	-	38	45
Aggregation degree, %	89	88	90	92	-	45	40
Properties of prepared matrix							
Matrix activity (800°C/4h)	17.2	15.3	12.2	10.2	15.5	16.0	9.1
Matrix strength, h ⁻¹	1.0	1.1	1.2	1.3	1.6	1.8	1.5

It can be seen from Table 1 that the phosphorus-alumina sols according to the present disclosure have QP_0^2/QP_0^0 values greater than those of the phosphorus-alumina sols from the comparative examples, indicating a higher ratio of the amount of polyphosphate to the amount of free phosphate, and also have small average colloidal particle sizes with uniform distribution and high aggregation degrees. By comparing Example 1 with Comparative Example 1 and Comparative Example 2, it can be seen that, at the same or higher P/Al ratio, the matrix prepared from the phosphorus-alumina sol according to the present disclosure has higher activity and lower strength, indicating fewer free phosphate, less impact on the matrix, and better binding properties.

Examples A1-6 are preparation examples of catalysts CAT-A1 to CAT-A6.

Example A1

a) P-β molecular sieve and MPZ molecular sieve were weighed, added to decaionized water, and slurried for 20 min to obtain a molecular sieve slurry.

Kaolin, alumina sol, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and pseudo-boehmite were added to decationized water and slurried for 20 min. The molecular sieve slurry was added under stirring. Hydrochloric acid was added to adjust the pH of the slurry to 3.0, and then slurring was continued for 45 min to obtain a first
5 slurry.

b) The phosphorus-alumina sol P-1 was added to the first slurry obtained in step a), stirred for 5 min to obtain a second slurry. The second slurry was spray-dried to obtain microspheres, and the microspheres were calcined at 500°C for 2 hours to obtain catalyst CAT-A1. The material proportions and
10 catalyst parameters are shown in Table 2.

Examples A2-A6

Examples A2-A6 followed the same procedure as Example A1 but with different material proportions to prepare catalysts CAT-A2 to CAT-A6. The
15 material proportions and catalyst parameters are shown in Table 2.

Comparative Example A1

MPZ molecular sieve, kaolin, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and pseudo-boehmite were weighed, added to decationized water and alumina sol, and slurried for 120
20 minutes. Hydrochloric acid was added to adjust the pH of the slurry to 3.0, and then slurring was continued for 45 min. Phosphorus-alumina sol DP-1 was added, and after stirring for 5 min, the obtained slurry was spray-dried to obtain microspheres, and the microspheres were calcined at 500°C for 1 hour to obtain catalyst DCAT-A1. The material proportions and catalyst parameters are
25 shown in Table 2.

Comparative Example A2

Comparative Example A2 followed the same procedure as Example A1 to prepare catalyst DCAT-A2, except that the phosphorus-alumina sol P-1 was
30 replaced with the phosphorus-alumina sol DP-1. The material proportions and catalyst parameters are shown in Table 2.

Comparative Example A3

Comparative Example A3 followed the same procedure as Example A1 to prepare catalyst DCAT-A3, except that, as shown in Table 2, the P- β molecular sieve in step a) was replaced with an equal amount of MPZ molecular sieve.

5 The material proportions and catalyst parameters are shown in Table 2.

Table 2.

	Ex. A1	Ex. A2	Ex. A3	Ex. A4	Ex. A5	Ex. A6	CE. A3	CE. A1	CE. A2
Catalyst No.	CAT-A1	CAT-A2	CAT-A3	CAT-A4	CAT-A5	CAT-A6	DCAT-A3	DCAT-A1	DCAT-A2
P- β molecular sieve	5	15	30	25	5	5	/	/	5
MPZ molecular sieve	50	40	25	25	50	50	55	55	50
Kaolin	9	8	5	6	10	9	9	9	9
Phosphorus-alumina binder	P-1	P-2	P-3	P-4	P-1	P-3	P-1	DP-1	DP-1
Phosphorus-alumina binder, as Al ₂ O ₃ and P ₂ O ₅	22	20	24	27	6	22	22	22	22
Pseudo-boehmite, as Al ₂ O ₃	6	8	5	8	12	6	6	6	6
Alumina sol, as Al ₂ O ₃	7	7	8	7	12	7	7	7	7
FeCl ₃ ·6H ₂ O, as Fe ₂ O ₃	1	2	3	2	5	1	1	1	1
Total	100	100	100	100	100	100	100	100	100
Total phosphorus content in catalyst, wt%, as P ₂ O ₅	17.42	17.61	21.80	26.40	7.61	20.54	17.47	17.63	17.58
Metal content in catalyst, wt%, as Fe ₂ O ₃	1.10	2.08	3.05	2.05	5.10	2.10	1.11	1.11	1.10
Pore volume of catalyst by BJH method, mL/g	0.124	0.128	0.132	0.130	0.122	0.123	0.118	0.117	0.121

Examples B1-6 are preparation examples of catalysts CAT-B1 to CAT-B6.

Example B1

a) MPZ molecular sieve was weighed, added to decationized water, and

slurried for 20 min to obtain a molecular sieve slurry. Kaolin, macroporous alumina material, alumina sol, and pseudo-boehmite were added to decaionized water and slurried for 20 min. The molecular sieve slurry was added under stirring. Hydrochloric acid was added to adjust the pH of the
5 slurry to 3.0, and then slurring was continued for 45 min to obtain a first slurry.

b) The phosphorus-alumina sol P-1 was added to the first slurry obtained in step a), stirred for 5 min to obtain a second slurry. The second slurry was spray-dried to obtain microspheres, and the microspheres were calcined at
10 500°C for 2 hours to obtain catalyst CAT-B1. The material proportions and catalyst parameters are shown in Table 3.

Examples B2-B6

Examples B2-B6 followed the same procedure as Example B1 but with
15 different material proportions to prepare catalysts CAT-B2 to CAT-B6. The material proportions and catalyst parameters are shown in Table 3.

Comparative Example B1

MPZ molecular sieve, kaolin, and pseudo-boehmite were weighed, added
20 to decaionized water and alumina sol, and slurried for 120 min. Hydrochloric acid was added to adjust the pH of the slurry to 3.0, and then slurring was continued for 45 min. Phosphorus-alumina sol DP-1 was added, and after stirring for 5 min, the obtained slurry was spray-dried to obtain microspheres, and the microspheres were calcined at 500°C for 1 hour to obtain catalyst
25 DCAT-B1. The material proportions and catalyst parameters are shown in Table 3.

Comparative Example B2

Comparative Example B2 followed the same procedure as Example B1 to
30 prepare catalyst DCAT-B2, except that the phosphorus-alumina sol P-1 was replaced with the phosphorus-alumina sol DP-1. The material proportions and catalyst parameters are shown in Table 3.

Comparative Example B3

Comparative Example B3 followed the same procedure as Example B1 to prepare catalyst DCAT-B3, except that no macroporous alumina material was added. The material proportions and catalyst parameters are shown in Table 3.

5

Table 3.

	Ex. B1	Ex. B2	Ex. B3	Ex. B4	Ex. B5	Ex. B6	CE. B1	CE. B2	CE. B3
Catalyst No.	CAT-B1	CAT-B2	CAT-B3	CAT-B4	CAT-B5	CAT-B6	DCAT-B1	DCAT-B2	DCAT-B3
MPZ molecular sieve	45	45	50	55	45	45	45	45	45
Macroporous alumina material, on dry basis	6	8	10	4	21	6	/	6	/
Kaolin	10	8	2	4	10	10	16	10	16
Phosphorus-alumina binder	P-1	P-2	P-3	P-4	P-2	P-3	DP-1	DP-1	P-1
Phosphorus-alumina binder, as Al ₂ O ₃ and P ₂ O ₅	22	26	26	22	6	22	22	22	22
Pseudo-boehmite, as Al ₂ O ₃	10	6	4	6	8	10	10	10	10
Alumina sol, as Al ₂ O ₃	7	7	8	7	10	7	7	7	7
Total	100	100	100	100	100	100	100	100	100

Examples 5-6 are preparation examples of the porous silica-alumina composite material of the present disclosure.

10

Example 5

Preparation of directing agent: 245 g of sodium silicate solution (containing 20.65 wt% SiO₂, 5.25 wt% Na₂O) was weighed, and 118 g of sodium aluminate solution (containing 3.22 wt% Al₂O₃, 20.7 wt% Na₂O) was

slowly added under rapid stirring, stirred for 1 hour, and aged at room temperature for 48 hours to obtain a directing agent.

(1) 100 g (on dry basis) of kaolin was calcined at 800°C for 2 h to obtain metakaolin, which was then treated with 2 L of 3 mol/L hydrochloric acid under stirring at 85°C for 1 h, followed by filtration and washing to obtain a first mixture.

(2) Under stirring, the first mixture obtained in step (1) was mixed with 415 g of sodium silicate solution (containing 20.65 wt% SiO₂, 5.25 wt% Na₂O), 60 g of the directing agent, and 98 g of 5 wt% sodium hydroxide solution to obtain a second mixture. The second mixture had a composition with a weight ratio of 0.69Na₂O : Al₂O₃ : 3.27SiO₂ : 9.78H₂O.

(3) The second mixture was heated to 92°C, stirred at constant temperature, and subjected to hydrothermal crystallization for 20 hours. After crystallization, the crystallization tank was quenched, and the content thereof was filtered and washed with water until the pH of the washings was less than 10, and then dried at 120°C for 2 hours to obtain a porous silica-alumina composite material Y1. Its property parameters are shown in Table 4.

Example 6

(1) 100 g (on dry basis) of kaolin was calcined at 900°C for 2 h to obtain metakaolin, which was then treated with 2 L of 3 mol/L hydrochloric acid under stirring at 90°C for 1.5 h, followed by filtration and washing to obtain a first mixture.

(2) Under stirring, the first mixture obtained in step (1) was mixed with 450 g of sodium silicate solution (containing 20.65 wt% SiO₂, 5.25 wt% Na₂O), 60 g of the directing agent (the same directing agent as used in Example 5), and 120 g of 5 wt% sodium hydroxide solution to obtain a second mixture. The second mixture had a composition with a weight ratio of 0.75Na₂O : Al₂O₃ : 3.43SiO₂ : 10.81H₂O.

(3) The second mixture was heated to 95°C, stirred at constant temperature, and subjected to hydrothermal crystallization for 28 hours. After crystallization, the crystallization tank was quenched, and the content thereof

was filtered and washed with water until the pH of the washings was less than 10, and then dried at 120°C for 2 hours to obtain a porous silica-alumina composite material Y2. Its property parameters are shown in Table 4.

Table 4.

	Sample No.	Specific surface area, m ² /g	Total pore volume, mL/g	Meso-macroporous ratio [※] , %	Composition (mass ratio)
Ex. 5	Y-1	351.09	0.16	21.84	0.13Na ₂ O : Al ₂ O ₃ : 2.48SiO ₂
Ex. 6	Y-2	497.39	0.25	29.69	0.18Na ₂ O : Al ₂ O ₃ : 2.67SiO ₂

※Meso-macroporous ratio: proportion of the volume of meso-macropores with a pore size of 2-50 nm to the total pore volume.

Examples C1-6 are preparation examples of catalysts CAT-C1 to CAT-C6.

Example C1

a) MPZ molecular sieve was weighed, added to decationized water, and slurried for 20 min to obtain a molecular sieve slurry. Kaolin, porous silica-alumina composite material, alumina sol, and pseudo-boehmite were added to decationized water and slurried for 20 min. The molecular sieve slurry was added under stirring. Hydrochloric acid was added to adjust the pH of the slurry to 3.0, and then slurring was continued for 45 min to obtain a first slurry.

b) The phosphorus-alumina sol P-1 was added to the first slurry obtained in step a), stirred for 5 min to obtain a second slurry. The second slurry was spray-dried to obtain microspheres, and the microspheres were calcined at 500°C for 2 hours to obtain catalyst CAT-C1. The material proportions and catalyst parameters are shown in Table 5.

Examples C2-C6

Examples C2-C6 followed the same procedure as Example C1 but with different material proportions to prepare catalysts CAT-C2 to CAT-C6. The

material proportions and catalyst parameters are shown in Table 5.

Comparative Example C1

MPZ molecular sieve, kaolin, and pseudo-boehmite were weighed, added
 5 to decationized water and alumina sol, and slurried for 120 min. Hydrochloric acid was added to adjust the pH of the slurry to 3.0, and then slurring was continued for 45 min. Phosphorus-alumina sol DP-1 was added, and after stirring for 5 min, the obtained slurry was spray-dried to obtain microspheres, and the microspheres were calcined at 500°C for 1 hour to obtain DCAT-C1.
 10 The material proportions and catalyst parameters are shown in Table 5.

Comparative Example C2

Comparative Example C2 followed the same procedure as Example C1 to prepare catalyst DCAT-C2, except that the phosphorus-alumina sol P-1 was
 15 replaced with the phosphorus-alumina sol DP-1. The material proportions and catalyst parameters are shown in Table 5.

Comparative Example C3

Comparative Example C3 followed the same procedure as Example C1 to
 20 prepare catalyst DCAT-C3, except that no porous silica-alumina composite material was added. The material proportions and catalyst parameters are shown in Table 5.

Table 5.

	Ex. C1	Ex. C2	Ex. C3	Ex. C4	Ex. C5	Ex. C6	CE. C1	CE. C2	CE. C3
Catalyst No.	CAT-C1	CAT-C2	CAT-C3	CAT-C4	CAT-C5	CAT-C6	DCAT-C1	DCAT-C2	DCAT-C3
MPZ molecular sieve	40	45	40	50	40	40	40	40	40
Porous silica-alumina composite material	Y1	Y2	Y1	Y2	Y2	Y2	/	Y1	/
Porous silica-alumina	15	10	20	10	28	15	/	15	/

composite material, on dry basis									
Kaolin	10	10	9	3	10	10	25	10	25
Phosphorus-alumina binder	P-1	P-2	P-3	P-4	P-1	P-3	DP-1	DP-1	P-1
Phosphorus-alumina binder, as P ₂ O ₅ and Al ₂ O ₃	22	22	18	24	6	22	22	22	22
Pseudo-boehmite	6	6	6	6	6	6	6	6	6
Alumina sol, as Al ₂ O ₃	7	7	7	7	10	7	7	7	7
Total	100	100	100	100	100	100	100	100	100

The following test examples, exemplified by using a fixed fluidized bed reactor, illustrate the catalytic cracking effect of the catalyst according to the present disclosure.

5

Test Example A

The catalytic cracking procatalyst SLA-1 and 30 g each of CAT-A1~6 and DCAT-A1~3 were aged at 800°C under 100% water vapor atmosphere for 17 hours, respectively. Different amounts of the aged catalysts were taken respectively and mixed with SLA-1 (properties thereof shown in Table 6). The catalyst mixtures were charged into a reactor of a small fixed fluidized bed reaction apparatus to catalytically crack the feedstock oil shown in Table 7. Table 8 shows the reaction conditions used and evaluation results.

15

Table 6. Properties of catalytic cracking procatalyst SLA-1

Item	Value
Crystallinity, wt%	15
BET specific surface area, m ² /g	181
Al ₂ O ₃ , wt%	53.8
SiO ₂ , wt%	37.9

Na ₂ O, wt%	0.0710
Fe ₂ O ₃ , wt%	0.629
P ₂ O ₅ , wt%	0.505
Re ₂ O ₃ , wt%	4.32
Pore volume, mL/g	0.36
Attrition index, %(mass fraction)/h	1.8
Apparent bulk density, g/mL	0.75
Micro-activity index (800°C/17h), %(mass fraction)	62

Table 7. Properties of feedstock oil for evaluation

Component Name	Standard oil
Viscosity at 80°C, mm ² /s	19.24
Viscosity at 100°C, mm ² /s	11.23
Solidification Point, °C	40
Saturated hydrocarbons, wt%	62.3
Aromatics, wt%	22.7
Resins, wt%	14.4
Asphaltenes, wt%	0.6
Carbon residue, wt%	3.11
Density at 20°C, kg/m ³	910.4
Initial boiling point, °C	267
5%(φ), °C	318
10%(φ), °C	339
30%(φ), °C	407
50%(φ), °C	451
70%(φ), °C	494
Final boiling point yield, %(φ)	81.5
Final boiling point temperature, °C	540
Sulfur content, wt%	0.61
Carbon content, wt%	86.9

Hydrogen content, wt%	12.63
Nitrogen content, %	0.2

Table 8. Evaluation results of CAT-A1~6 and DCAT-A1~3

	Ex. A1	Ex. A2	Ex. A3	Ex. A4	Ex. A5	Ex. A6	CE. A3	CE. A1	CE. A2
Catalyst	5%CA	5%CA	5%CA	5%CA	5%CA	5%CA	5%DC	5%DC	5%DC
	T-A1	T-A2	T-A3	T-A4	T-A5	T-A6	AT-A3	AT-A1	AT-A2
	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL
	A-1	A-1	A-1	A-1	A-1	A-1	A-1	A-1	A-1
Reaction temperature, °C	530	530	530	530	530	530	530	530	530
Space velocity, h ⁻¹	8	8	8	8	8	8	8	8	8
Catalyst-to-oil ratio (by weight)	6	6	6	6	6	6	6	6	6
Material balance, wt%									
Dry gas	3.19	3.33	2.7	2.76	2.86	2.91	2.69	2.66	2.68
Liquefied gas	23.84	23.07	23.17	22.42	23.19	23.47	23.12	23.05	23.15
C5+ gasoline	42.3	43.58	44.61	45.82	42.71	42.59	42.32	42.27	42.56
Diesel	16.37	15.73	15.55	14.89	16.32	16.25	16.54	16.78	16.41
Heavy oil	8.35	8.23	7.93	8.13	8.71	8.64	8.98	8.79	8.92
Coke	5.95	6.06	6.04	5.98	6.21	6.14	6.35	6.45	6.28
Conversion, wt%	75.28	76.04	76.52	76.98	74.97	75.11	74.48	74.43	74.67
Gasoline + LPG	66.14	66.65	67.78	68.24	65.90	66.06	65.44	65.32	65.71
Slurry oil + Diesel	24.72	23.96	23.48	23.02	25.02	24.79	25.52	25.57	25.33
Propylene, wt%	9.27	8.96	8.69	7.82	8.92	9.05	8.82	8.75	8.65
Butylene, wt%	7.72	7.81	7.85	7.98	7.39	7.42	7.21	7.18	7.36
Propylene/Liquefied gas, %	38.88	38.84	37.51	34.88	38.46	38.56	38.15	37.96	37.37
Butylene/Liquefied gas, %	32.38	33.85	33.88	35.59	31.87	31.61	31.19	31.15	31.79

Olefin content in LPG, %	71.27	72.69	71.39	70.47	70.33	70.17	69.33	69.11	69.16
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It can be seen from Table 8 that, compared with the catalysts from comparative examples, the catalysts according to the present disclosure enable to effectively increase the content of propylene and butylene in catalytic cracking liquefied gas, increase the olefin content in LPG, reduce the sum of the yields of diesel and slurry oil, and increase the sum of the yields of gasoline and LPG.

Test Example B

The catalytic cracking procatalyst SLA-2 and 30 g each of CAT-B1~6 and DCAT-B1~3 were aged at 800°C under 100% water vapor atmosphere for 17 hours, respectively. Different amounts of the aged catalysts were taken respectively and mixed with SLA-2 (properties thereof shown in Table 9). The catalyst mixtures were charged into a reactor of a small fixed fluidized bed reaction apparatus to catalytically crack the feedstock oil shown in Table 10. Table 11 shows the reaction conditions used and reaction results.

Table 9. Properties of catalytic cracking procatalyst SLA-2

Item	Value
Micro-activity, %(mass fraction)	57
Rare earth oxide, wt%	2.2
Bulk density, g/mL	0.8
Copper content, mg/kg	<0.05
Iron content, mg/kg	3460
Sodium content, mg/kg	2000
Nickel content, mg/kg	3860
Vanadium content, mg/kg	8340
Pore volume, mL/g	0.14
Specific surface area, m ² /g	103

<20 μm , %(volume fraction)	1.04
20-40 μm , %(volume fraction)	12.71
40-80 μm , %(volume fraction)	61.89
80-110 μm , %(volume fraction)	20.67
>110 μm , %(volume fraction)	3.69

Table 10. Properties of feedstock oil for evaluation

Density (20°C), g/cm ³	0.92
Carbon residue, %(mass fraction)	4.81
Initial boiling point, °C	228.00
Distillate at 500°C, %(volume fraction)	44.50
Distillate at 538°C, %(volume fraction)	54.50
Asphaltene content, %(mass fraction)	1.73
Saturated hydrocarbon content, %(mass fraction)	58.17
Aromatic content, %(mass fraction)	29.01
Resin content, %(mass fraction)	11.10
Total nitrogen, mg/kg	594.30
Iron content, mg/kg	2.16
Sodium content, mg/kg	1.39
Nickel content, mg/kg, ≤ 10	6.44
Vanadium content, mg/kg, ≤ 10	8.91

Table 11. Evaluation results of CAT-B1~6 and DCAT-B1~3

	Ex. B1	Ex. B2	Ex. B3	Ex. B4	Ex. B5	Ex. B6	CE. B1	CE. B2	CE. B3
Catalyst	5%CA	5%CA	5%CA	5%CA	5%CA	5%CA	5%DC	5%DC	5%DC
	T-B1	T-B2	T-B3	T-B4	T-B5	T-B6	AT-B1	AT-B2	AT-B3
	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL
	A-2	A-2	A-2	A-2	A-2	A-2	A-2	A-2	A-2
Reaction temperature, °C	530	530	530	530	530	530	530	530	530

Space velocity, h ⁻¹	8	8	8	8	8	8	8	8	8
Catalyst-to-oil ratio (by weight)	6	6	6	6	6	6	6	6	6
Material balance, wt%									
Dry gas	2.96	2.97	3.11	3.15	2.91	2.98	2.97	2.89	2.95
Liquefied gas	19.29	19.42	20.69	20.43	19.01	19.17	18.62	18.31	18.66
Gasoline	39.46	39.24	38.11	37.93	39.59	39.63	39.02	39.92	39.31
Diesel	18.53	18.61	18.38	18.65	18.77	18.45	18.79	18.63	18.45
Slurry oil	9.88	9.78	9.76	9.99	9.92	9.95	10.35	10.10	10.45
Coke	9.88	9.98	9.95	9.84	9.79	9.82	10.26	10.15	10.17
Conversion, wt%	71.59	71.61	71.86	71.35	71.30	71.60	70.87	71.27	71.10
Propylene, wt%	7.17	7.28	7.78	8.12	6.96	7.09	6.53	6.63	6.82
Total liquid yield	77.27	77.28	77.18	77.01	77.37	77.25	76.43	76.86	76.43
Propylene/Liquefied gas, %	37.20	37.47	37.61	39.75	36.63	36.97	35.08	36.22	36.54

It can be seen from Table 11 that, compared with the catalysts from comparative examples, the catalysts according to the present disclosure enable to effectively increase the yields of catalytic cracking liquefied gas and propylene, with a higher propylene concentration in the liquefied gas, achieve a higher total liquid yield and lower yields of slurry oil and coke, significantly improving heavy oil cracking ability.

Test Example C

The catalytic cracking procatalyst SLA-2 and 30 g each of CAT-C1~6 and DCAT-C1~3 were aged at 800°C under 100% water vapor atmosphere for 17 hours, respectively. Different amounts of the aged catalysts were taken respectively and mixed with SLA-2 (properties thereof shown in Table 9). The catalyst mixtures were charged into a reactor of a small fixed fluidized bed reaction apparatus to catalytically crack the feedstock oil shown in Table 10.

Table 12 shows the reaction conditions used and reaction results.

Table 12. Evaluation results of CAT-C1~6 and DCAT-C1~3

	Ex. C1	Ex. C2	Ex. C3	Ex. C4	Ex. C5	Ex. C6	CE. C1	CE. C2	CE. C3
Catalyst	5%CA	5%CA	5%CA	5%CA	5%CA	5%CA	5%DC	5%DC	5%DC
	T-C1	T-C2	T-C3	T-C4	T-C5	T-C6	AT-C1	AT-C2	AT-C3
	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL	95%SL
	A-2	A-2	A-2	A-2	A-2	A-2	A-2	A-2	A-2
Reaction temperature, °C	530	530	530	530	530	530	530	530	530
Space velocity, h ⁻¹	8	8	8	8	8	8	8	8	8
Catalyst-to-oil ratio (by weight)	6	6	6	6	6	6	6	6	6
Material balance, wt%									
Dry gas	2.91	3.02	2.94	3.13	2.89	2.9	2.97	2.89	3.01
Liquefied gas	18.92	19.64	18.84	20.7	18.32	18.85	18.62	18.31	18.78
Gasoline	40.76	40.15	41.07	39.67	41.26	40.86	39.02	40.06	39.12
Diesel	17.35	17.46	17.57	17.34	17.45	17.43	18.79	18.63	18.57
Slurry oil	10.13	9.77	9.59	9.37	10.23	10.01	10.35	10.1	10.3
Coke	9.92	9.96	9.99	9.8	9.85	9.95	10.26	10.01	10.22
Conversion, wt%	72.51	72.77	72.84	73.3	72.32	72.56	70.87	71.27	71.13
Gasoline + LPG	59.68	59.79	59.91	60.37	59.58	59.71	57.64	58.37	57.9
Total liquid yield	77.03	77.25	77.48	77.71	77.03	77.14	76.43	77	76.47
Propylene, wt%	6.9	7.23	6.85	7.86	6.65	6.88	6.45	6.58	6.73
Propylene/Liquefied gas, %	36.47	36.81	36.36	37.97	36.30	36.50	34.64	35.94	35.84

5 It can be seen from Table 12 that, compared with the catalysts from comparative example, the catalyst compositions according to the present disclosure enable to increase the yield of propylene, achieve a high yield of

light oil (i.e., the total yield of gasoline and LPG), high total liquid yield and conversion, and lower coke yield, significantly improving heavy oil cracking ability and propylene selectivity.

5 The preferable embodiments of the present disclosure have been described in detail above with reference to the accompanying drawings. However, the present disclosure is not limited to the specific details of the above embodiments. Within the technical concept of the present disclosure, various simple modifications can be made to the technical solutions of the present disclosure, and these simple modifications all fall within the protection
10 scope of the present disclosure.

In addition, it should be noted that the various specific technical features described in the above specific embodiments can be combined in any suitable manner without contradiction. To avoid unnecessary repetition, the present disclosure does not separately describe various possible combinations.

15 Furthermore, the various different embodiments of the present disclosure can be combined arbitrarily as long as such a combination does not deviate from the idea of the present disclosure, and should also be regarded as the content disclosed by the present disclosure.

CLAIMS

1. A phosphorus-alumina sol, the phosphorus-alumina sol comprising Al, P, and a stabilizer, and having a P/Al weight ratio of 1.6-6 : 1; wherein the phosphorus-alumina sol exhibits a ^{31}P NMR spectrum, with the resonance signal peak area at a chemical shift of -12 ± 2 ppm designated as QP_0^2 and the resonance signal peak area at a chemical shift of 0 ± 2 ppm designated as QP_0^0 , $\text{QP}_0^2/\text{QP}_0^0 = 1.5-5$, and the phosphorus-alumina sol has an average colloidal particle size of 10-30 nm.

2. The phosphorus-alumina sol according to claim 1, wherein, based on the total weight of the phosphorus-alumina sol, the phosphorus-alumina sol comprises Al in an amount, calculated as Al_2O_3 , of 3-15 wt%, P in an amount, calculated as P_2O_5 , of 15-40 wt%, and a stabilizer in an amount of 0.1-10 wt%; preferably, the phosphorus-alumina sol comprises Al in an amount, calculated as Al_2O_3 , of 3-12 wt%, P in an amount, calculated as P_2O_5 , of 15-35 wt%, and a stabilizer in an amount of 0.5-5 wt%; and/or

pH value of the phosphorus-alumina sol is in a range of 0.5-2.5; and/or
the solid content of the phosphorus-alumina sol is in a range of 15-50 wt%;
and/or

dynamic viscosity of the phosphorus-alumina sol is in a range of 10-50 cP.

3. The phosphorus-alumina sol according to claim 1 or 2, wherein, the stabilizer is a weakly acidic organic acid, preferably selected from at least one of glycolic acid, oxalic acid, acetic acid, malonic acid, malic acid, tartaric acid, succinic acid, adipic acid, maleic acid, itaconic acid, and citric acid, preferably oxalic acid, acetic acid, citric acid, or a combination thereof; and/or

the molar ratio of organic acid radicals of the stabilizer to Al is in a range of 0.05-0.5 : 1.

4. A method for preparing the phosphorus-alumina sol according to any one of claims 1-3, comprising:

1) under stirring at a temperature of 50°C - 95°C , mixing an aluminum salt source, decationized water, and a stabilizer to form a slurry, so as to obtain an

alumina precursor solution.

2) under stirring at a temperature of 25°C-70°C, adding a phosphate to the alumina precursor solution at a P/Al weight ratio of 1.6-6 : 1 for reaction, so as to obtain a phosphorus-alumina sol.

5 5. The method according to claim 4, wherein the aluminum salt source is selected from one or more of aluminum nitrate, aluminum sulfate, and aluminum chloride; and/or

the pH value of the alumina precursor solution is in a range of 0.5-3.0; and/or

10 the solid content of the alumina precursor solution is in a range of 5-40 wt%; and/or

the phosphate is diammonium hydrogen phosphate and/or ammonium dihydrogen phosphate; and/or

in step 1), the slurry mixing time is in a range of 10-50 minutes; in step 15 2), the reaction time is in a range of 10-60 minutes.

6. A hydrocarbon oil conversion catalyst, the catalyst comprising a molecular sieve, a phosphorus-alumina binder, other inorganic binder(s) different from the phosphorus-alumina binder, an optional metal component, an optional meso-macroporous inorganic oxide material, and an optional clay, 20 wherein the phosphorus-alumina binder is derived from the phosphorus-alumina sol according to any one of claims 1-3 or the phosphorus-alumina sol prepared by the method according to any one of claims 4-5.

7. The catalyst according to claim 6, wherein, based on the dry weight of the catalyst, the catalyst comprises the molecular sieve in an amount of 25- 25 75 wt%, preferably 30-65 wt%, the metal component in an amount, calculated as metal oxide, of 0.5-8 wt%, preferably 0.8-6 wt%, the phosphorus-alumina binder in an amount, calculated as oxide, of 3-40 wt%, preferably 8-32 wt%, the other inorganic binder(s) in an amount, calculated as oxide, of 1-25 wt%, preferably 2-20 wt%, and the clay in an amount of 0-30 wt%, preferably 1-25 30 wt%; and/or

wherein the molecular sieve comprises an MFI molecular sieve and a BEA molecular sieve, the molecular sieve comprises a first phosphorus component,

the phosphorus-alumina binder comprises a second phosphorus component, and the total content of the first phosphorus component and the second phosphorus component in the catalyst, calculated as P_2O_5 , is in a range of 10-35 wt%; and/or

5 wherein the catalyst has a pore volume determined by BJH method of greater than 0.12 mL/g; and/or

wherein the metal in the metal component is selected from at least one of Group VIII metals, preferably one or more of Fe, Co, and Ni.

8. The catalyst according to claim 6, wherein the meso-macroporous
10 inorganic oxide material is a macroporous alumina material, and the molecular sieve is an MFI molecular sieve;

based on the dry weight of the catalyst, the catalyst comprises the MFI molecular sieve in an amount of 10-75 wt%, preferably 15-65 wt%, the macroporous alumina material in an amount of 1-30 wt%, preferably 2-25 wt%,
15 the phosphorus-alumina binder in an amount, calculated as oxide, of 3-35 wt%, preferably 8-32 wt%, the other inorganic binder(s) in an amount, calculated as oxide, of 1-20 wt%, preferably 2-20 wt%, and the clay in an amount of 0-60 wt%, preferably 1-25 wt%; and/or

the macroporous alumina material has a bimodal pore distribution
20 structure, with the pore volume of pores having a pore size of 2-10 nm accounting for 20-40% of the total pore volume, and the pore volume of pores having a pore size of 10-100 nm accounting for 60-80% of the total pore volume; and/or

the MFI molecular sieve is selected from one or more of a hydrogen-form
25 MFI molecular sieve, a phosphorus-containing MFI molecular sieve, and a transition metal-containing MFI molecular sieve.

9. The catalyst according to claim 6, wherein the meso-macroporous inorganic oxide material is a porous silica-alumina composite material, and the molecular sieve is an MFI molecular sieve;

30 based on the dry weight of the catalyst, the catalyst comprises the MFI molecular sieve in an amount of 10-75 wt%, preferably 15-65 wt%, the porous silica-alumina composite material in an amount of 1-30 wt%, preferably 2-25

wt%, the phosphorus-alumina binder in an amount, calculated as oxide, of 3-35 wt%, preferably 8-32 wt%, the other inorganic binder(s) in an amount, calculated as oxide, of 1-20 wt%, preferably 2-20 wt%, and the clay in an amount of 0-60 wt%, preferably 1-25 wt%; and/or

5 the porous silica-alumina composite material has a mass composition of $(0.01-1)\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : (2-5)\text{SiO}_2$, a specific surface area of 300-600 m^2/g , a total pore volume of 0.15-0.4 mL/g, and a pore volume of meso-macropores having a pore size of 2-50 nm accounting for 20-40% of the total pore volume; and/or

10 the MFI molecular sieve is selected from one or more of a hydrogen-form MFI molecular sieve, a phosphorus-containing MFI molecular sieve, and a transition metal-containing MFI molecular sieve.

10. The catalyst according to any one of claims 6-9, wherein the other inorganic binder(s) is selected from one or more of pseudo-boehmite, acidified
15 pseudo-boehmite, alumina sol, silica-alumina sol, and silica sol; and/or

the clay is selected from one or more of kaolin, sepiolite, attapulgite, rectorite, montmorillonite, and diatomite.

11. A method for preparing the catalyst according to any one of claims 6-10, the method comprising:

20 a) mixing the molecular sieve, the other inorganic binder(s), a metal source of the optional metal component, the optional meso-macroporous inorganic oxide material, the optional clay, and water to form a slurry, controlling pH value of the slurry to be greater than 2.5, so as to obtain a first slurry;

25 b) mixing the first slurry with the phosphorus-alumina sol to obtain a second slurry, followed by spray drying and calcination, so as to obtain the catalyst.

12. The method according to claim 11, wherein the metal source is a soluble salt of a metal selected from at least one of Group VIII metals,
30 preferably one or more of an iron salt, a cobalt salt, and a nickel salt, more preferably $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; and/or

the spray drying is conducted at an inlet temperature of 300-700°C, and

an outlet temperature of 80-200°C; and/or

the calcination is conducted at a temperature of 400-700°C, for a time of 0.5-100 hours.

13. A catalyst composition, the catalyst composition comprising a cocatalyst and an optional procatalyst, wherein the cocatalyst is the catalyst according to any one of claims 6-10, and the optional procatalyst preferably is a catalytic cracking catalyst.

14. A hydrocarbon oil catalytic conversion method, comprising bringing a hydrocarbon oil into contact with the catalyst according to any one of claims 6-10 or the catalyst composition according to claim 13 for reaction.

15. The method according to claim 14, wherein the reaction is conducted under conditions including: a temperature of 300-700°C, a weight hourly space velocity of 4-120 h⁻¹, and a catalyst-to-oil ratio by weight of 1-20.