

CLAIMS

1. A hydrocracking catalyst for hydrocarbon oil comprising a hydrogenative metal component carried on a support containing an ultra-stable Y-type zeolite, wherein the above ultra-stable Y-type zeolite is a framework-substituted zeolite (hereinafter referred to as a framework-substituted zeolite-1) in which a part of aluminum atoms constituting a zeolite framework thereof is substituted with 0.1-5 mass% zirconium atoms and 0.1-5 mass% titanium ions calculated on an oxide basis.
2. A hydrocracking catalyst for hydrocarbon oil according to Claim 1, wherein said zeolite-1 contains from 0.1 to 5 mass% hafnium atoms as calculated as the oxide basis.
3. The hydrocracking catalyst for hydrocarbon oil according to Claim 1, wherein the support contains the zeolite-1 and inorganic oxide excluding the zeolite-1.
4. The hydrocracking catalyst for hydrocarbon oil according to claim 3, wherein the inorganic oxide is alumina and /or silica-alumina.
5. The hydrocracking catalyst for hydrocarbon oil according to Claim 1, wherein the support further contains a titanium-substituted zeolite of which at least a part of aluminum atoms constituting a framework of the ultra-stable Y-type zeolite is substituted only with titanium atoms.
6. The hydrocracking catalyst for hydrocarbon oil according to Claim 5, wherein said framework-substituted zeolite-2 contains from 0.1 to 5 mass% titanium atoms as calculated as the oxide basis.
7. The hydrocracking catalyst for hydrocarbon oil according to Claim 5, wherein the support comprises the framework-zeolite-1, the framework-substituted zeolite-2 and inorganic oxide excluding the framework-substituted zeolite-1 and the framework-substituted zeolite-2.

8. The hydrocracking catalyst for hydrocarbon oil according to Claim 1, wherein the framework-zeolite-1 has the following characteristics:
 - (a) a crystal lattice constant of 2.430 to 2.450 nm,
 - (b) a specific surface area of 600 to 900 m²/g, and
 - (c) a molar ratio of SiO₂ to Al₂O₃ of 20 to 100.
9. The hydrocracking catalyst for hydrocarbon oil according to claim 8, having a specific surface area of 200 to 450 m²/g; a volume of pores having a diameter of 600 Å or less of 0.40 to 0.75 ml/g; and a carrying amount of a hydrogenative metal component falls of 0.01 to 40 mass%.
10. A method for hydrocracking hydrocarbon oil, comprising: hydrocracking hydrocarbon oil with the hydrocracking catalyst according to Claim 1.
11. The method for hydrocracking hydrocarbon oil according to Claim 10, further comprising:
 - filling a hydrotreating apparatus which is a flow reactor with the hydrocracking catalyst; and
 - treating a hydrocarbon oil having a boiling point of 375°C to 833°C in the presence of hydrogen at a reactor temperature of 300°C to 500°C, a hydrogen pressure of 4 to 30 MPa, a liquid hourly space velocity (LHSV) of 0.1 to 10 h⁻¹, and a hydrogen/oil ratio of 500 to 2500 Nm³/m³.
12. The method for hydrocracking hydrocarbon oil according to Claim 10, further comprising:
 - filling a hydrotreating apparatus which is a flow reactor with the hydrocracking catalyst; and
 - treating a hydrocarbon oil having a boiling point of 375°C to 650°C in the presence of hydrogen at a reactor temperature of 330°C to 450°C, a hydrogen pressure of 7 to 15 MPa, a liquid hourly space velocity (LHSV) of 0.2 to 1.5 h⁻¹, and a hydrogen/oil ratio of 1000 to 2000 Nm³/m³ to afford kerosene-gas oil.

13. The method for hydrocracking hydrocarbon oil according to Claim 11, wherein the flow reactor is a flow reactor selected from the group consisting of a stirred tank, a ebullient bed reactor, a baffled slurry tank, a fixed bed reactor, a rotating tubular reactor and a slurry-bed reactor.
14. The method for hydrocracking hydrocarbon oil according to claim 11, wherein the hydrocarbon oil comprises refined oil obtained from (1) crude oil, (2) synthetic crude oil, (3) bitumen, (4) oil sand, (5) shale oil or (6) coal oil.
15. The method for hydrocracking hydrocarbon oil according to claim 11, wherein the hydrocarbon oil comprises refined oil obtained from crude oil, synthetic crude oil, bitumen, oil sand, shale oil or coal oil, and said refined oil is a) vacuum gas oil (VGO) , b) deasphalted oil (DAO) obtained from a solvent deasphalting process or demetalized oil, c) light coker gas oil or heavy coker gas oil obtained from a coker process, d) cycle oil obtained from a fluid catalytic cracking (FCC) process or e) gas oil obtained from a visbraking process.
16. A method for producing a hydrocracking catalyst for hydrocarbon oil, the hydrocracking catalyst including a hydrogenative component carried on a support containing a framework-substituted zeolite-1 that contains zirconium atoms and/or hafnium atoms substituting a part of aluminum atoms forming a framework of an ultra-stable Y-type zeolite,

wherein the zeolite-1 is obtained by:

firing an ultra-stable Y-type zeolite at 500 °C. to 700 °C.,

the ultra-stable Y-type zeolite having a crystal lattice constant falling in a range of 2.430 or more and 2.450 nm or less, a specific surface area of 600 to 900 m²/g, and a molar ratio of SiO₂ to Al₂O₃ of 20 to 100;

forming a suspension containing the fired ultra-stable Y-type zeolite, the suspension having a liquid/solid mass ratio of 5 to 15;

adding inorganic acid or organic acid so that a pH of the above suspension is 1.0 to 2.0,

subsequently adding a zirconium compound, forming a mixture therefrom and neutralizing the said mixture.

17. The method for producing a hydrocracking catalyst for hydrocarbon oil according to claim 16, wherein the zeolite-1 is obtained by firing at 500 to 700 °C., an ultra-stable Y-type zeolite having a crystal lattice constant falling in a range of 2.430 nm or more and 2.450 nm or less, a specific surface area of 600 to 900 m²/g and a molar ratio of 20 to 100 in terms of SiO₂ to Al₂O₃, preparing a suspension having a mass ratio of 5 to 15 in terms of liquid/solid from the above fired ultra-stable Y-type zeolite, adding an inorganic acid or an organic acid thereto so that a pH of the above suspension is 1.0 to 2.0, subsequently adding a zirconium compound and/or a hafnium compound and a titanium compound forming a mixture therefrom and neutralizing the said mixture.