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(54) Titre : CATALYSEUR DE PRODUCTION D'OLEFINES LEGERES
(54) Title: CATALYST FOR THE PRODUCTION OF LIGHT OLEFINS

(57) Abrégé/Abstract:
The invention comprises a catalyst composition comprising a pentasil-type zeolite, one or more solid acidic promoters and optionally a filler and/or binder, methods for making the catalyst composition and a process for using the catalyst in the manufacture of olefins.

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(54) **Title:** CATALYST FOR THE PRODUCTION OF LIGHT OLEFINS

(57) **Abstract:** The invention comprises a catalyst composition comprising a pentasil-type zeolite, one or more solid acidic promoters and optionally a filler and/or binder, methods for making the catalyst composition and a process for using the catalyst in the manufacture of olefins.

CATALYST FOR THE PRODUCTION OF LIGHT OLEFINS

The present invention is related to a catalyst composition, a method or making the catalyst composition, and the use of the catalyst composition for the production of light olefins.

In recent years, there has been a tendency to utilize the fluid catalytic cracking process, not as a gasoline producer, but as a process to make light olefins for use as petrochemical materials or as building blocks for gasoline blending components, such as MTBE and alkylate.

The traditional method for the production of light olefins, such as ethylene, propylene, and butylene, from petroleum hydrocarbon is tubular furnace pyrolysis or pyrolysis over heat carrier or by catalytic conversion of lower aliphatic alcohol. More recently, the fluid catalytic cracking process employing small pore zeolite additives from the pentasil family is being used for the same at modern refinery. The small pore zeolite additives can be prepared as described in several patents (e.g. US 5, 472, 594, or WO98/41595).

Further descriptions of the production of light olefins by cracking processes are given in US Pat. No. 3,541,179; and JP No. 60-222 428.

The small pore zeolite additives are applied at the refinery by blending with the FCC host catalyst typically at 1-5 wt-% concentration. The obtained light olefin increase depends on the effectiveness of the additive, on the base catalyst formulation, feed type, and FCC process conditions, such as residence time and temperature. However, if the refiner targets a light olefin concentration, which is higher than that obtained at 1-5 wt-% intake of the small pore zeolite additive, usually the overall performance will start to deteriorate. This is because of a dilution of the host catalyst and increase in the bottoms conversion and saturation of the light olefins yield.

In one embodiment, the present invention is a catalyst composition comprising a pentasil-type zeolite, one or more solid acidic cracking promoters and, optionally, a filler and/or binder.

In a second embodiment, the present invention is a method of making the above catalyst composition, wherein an aqueous slurry comprising the pentasil-type zeolite and solid acidic cracking promoter(s) is prepared and dried.

In a third embodiment, the present invention is a process for producing olefins having up to about 12 carbon atoms per molecule, comprising contacting a petroleum feedstock at fluid catalytic cracking conditions with the above catalyst composition.

Other embodiments of the invention relate to details concerning catalyst composition, making the catalyst composition and use of the composition in making olefins.

The present invention describes FCC catalyst and catalyst/additive systems, which can be used to produce higher concentrations of olefins, particularly propylene, than obtained with the conventional additive systems as described above, and at the same time achieving high bottoms conversion. The systems are designed to function also in the processing of heavier feeds, which are especially sensitive to dilution effects when using the conventional catalyst/additive systems at higher additive concentrations. Hence, it is also an object of the systems of this invention not to suffer from dilution of the active ingredients and deterioration of the overall performance.

Particular achievements of the invention are:

- Effective ex-situ stabilization and/or modification of the small pore zeolite(s) in an additive/host and in catalyst particle system, in the presence of other active catalyst ingredients.
- Design of the additive/host and one particle catalyst system, which are highly active in upgrading the bottoms in gasoline and gas. The upgraded gasoline components are olefinic in nature. The active ingredients of the catalyst composition are selected in such a way that occurrence of hydrogen transfer and aromatization reactions, which are detrimental to the production of light olefins, are minimized.
- The additive/host or the one particle system, as prepared according to this patent, exhibits high bottoms conversion, in particular when very high quantities of the small pore zeolite are used in the blend.

The present invention describes catalyst compositions which exhibit improved activities and selectivities, as compared to the catalysts described in the prior art, for producing higher yields of light olefins, LCO, and gasoline, with minimum activities for hydrogen transfer reactions.

Preferably, the composition according to the invention does not comprise Rare Earth exchanged zeolite Y (REY, REHY, REUSY, REMgY), as these zeolites decrease olefin yields because of the high hydrogen transfer reaction activities.

Catalyst Composition of the Invention

As stated above, the catalyst composition of the invention comprises a pentasil-type zeolite and one or more solid acidic cracking promoters. The catalyst composition of the invention may comprise one or more additional materials selected from the group consisting of particle binders, diluents, fillers and extenders.

The pentasil-type zeolite is present in the catalyst composition in from about 5.0 wt% to about 80 wt%, preferably from about 5.0 to 40 wt%. The solid acidic cracking promoter is present in the catalyst composition in from about 5.0 wt% to about 80 wt%, preferably from about 10 to about 70 wt%. The weight ratio of said pentasil-type zeolite to solid acidic cracking promoter in the catalyst composition of the invention may be from about 0.03 to about 9.0.

The composition may comprise particles having average lengths along their major axis of from about 20 microns to about 200 microns, more preferably from about 30 microns to about 150 microns, and most preferably from about 40 to about 100 microns.

<u>The pentasil-type zeolite</u>

Pentasil-type zeolites include:

- zeolites selected from the group consisting of ITQ-type zeolite, beta zeolite and silicalite;
- ZSM-type zeolite;
- pentasil-type zeolites doped with a compound comprising a metal ion selected from the group consisting of ions of alkaline earth metals, transition metals, rare earth metals, phosphorous, boron, aluminum, noble metals and combinations thereof; and
- crystals having metals in tetrahedral coordination in the crystals selected from the group consisting of Al, As, B, Be, Co, Cr, Fe, Ga, Hf, In, Mg, Mn, Ni, P, Si, Ti, V, Zn, Zr and mixtures thereof.

The latter two groups being referred to as modified pentasil-type zeolites.

Pentasil-type zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, zeolite beta, zeolite boron beta, which are described in U.S. Patents

Nos. 3,308,069; 3,702,886; 3,709,979; 3,832,449; 4,016,245; 4,788,169; 3,941,871; 5,013,537; 4,851,602; 4,564,511; 5,137,706; 4,962,266; 4,329,328; 5,354,719; 5,365,002; 5,064,793; 5,409,685; 5,466,432; 4,968,650; 5,158,757; 5,273,737; 4,935,561; 4,299,808; 4,405,502; 4,363,718; 4,732,747; 4,828,812; 5,466,835; 5,374,747; and 5,354,875. Metals in tetrahedral coordination in the zeolite crystals include: Al, As, B, Be, Co, Cr, Fe, Ga, Hf, In, Mg, Mn, Ni, P, Si, Ti, V, Zn, Zr.

The pentasil-type zeolite may be doped with a compound comprising a metal ion selected from the group consisting of alkaline earth metal ions, transition metal ions, rare earth metal ions, phosphorous-containing ions, boron-containing ions, aluminum ions, noble metal ions and combinations thereof. The pentasil-type zeolite may be doped by any of the following methods:

- ion exchange of a pentasil-type zeolite the desired metal ion;
- preparing the pentasil-type zeolite by using seeds doped with the desired metal ion;
- preparing the pentasil-type zeolite by using reactants doped with the desired metal ion; or
- preparing the pentasil-type zeolite by using a reaction mixture comprising the precursor(s) of the pentasil-type zeolite and the desired metal ion.

The modified pentasil-type zeolites can be mixed with regular pentasil-type zeolites (i.e., ZSM type zeolite, zeolite beta, etc.) or with ion exchanged forms of pentasil-type zeolites, e.g. pentasil-type zeolites exchanged with transition metals.

<u>The Acidic Cracking Promotor Components</u>

The solid acidic materials provide an additional higher acidic function to the catalytic cracking particle which supplements the function of the pentasil-type zeolite component and synergistically, through the cracking process, produce higher yields of light olefins (i.e., ethylene, propylene, butylene, and pentenes).

Solid acid cracking promoters include zeolitic and non-zeolitic solid acids, with non-zeolitic solid acids being preferred.
More preferably, the solid acid cracking promoter is a high surface area non-zeolitic solid acid, the BET surface area being preferably above 200 m^2/g, more preferably between 250 and 400 m^2/g.

Examples of non-zeolitic solid acidic cracking promoters are alumina modified by incorporation of acid centers thereon or therein, acidic silica-alumina co-gels, acidic natural or synthetic clays, acidic titania, acidic zirconia, acidic titania-alumina, and co-gels of titania, alumina, zirconia, phosphates, borates, aluminophosphates, tungstates, molybdates and mixtures thereof. The acid centers may be selected from the group consisting of halides, sulfates, nitrates, titanates, zirconates, phosphates, borates, silicates and mixtures thereof. The solid acidic cracking promoter may comprise acidic silica-alumina, titania-alumina, titania/zirconia, alumina/zirconia or aluminum phosphate co-gels modified by the incorporation therein of metal ions or compounds selected from the group consisting of alkaline earth metals, transition metals, rare earth metals and mixtures thereof. The acidic silica-alumina co-gels may have been subjected to hydrothermal treatment.

The solid acidic cracking promoter may comprise a co-gel of an aluminium phosphate modified alumina or aluminum phosphate that has been doped with an acidic compound.

The acidic natural or synthetic clays may have been modified by calcining, steaming, dealumination, desilification, ion exchange, pillaring, exfoliation or combinations thereof.

The acidic titania, acidic zirconia, or both may be doped with sulfates, vanadates, phosphates, tungstates, borates, iron, rare earth metals or mixtures thereof.

The acidic zeolite materials may be selected from the group consisting of mordenite, zeolite Beta, NaY zeolite and USY zeolite that is dealuminated or ion exchanged with transition metals or both. The preferred transition metal is vanadium.

Zeolitic solid acidic cracking components include hydrogen modernite, dealuminated Y zeolites such as DAYs, high SAR USY dealuminated zeolites as used in hydrocracking, aluminum exchanged zeolites, LZ-210, aluminum exchanged USY, transition metal ion exchanged Y, USY, DAY zeolites.

Particularly preferred solid acidic cracking promoters are rare earth and/or silica doped aluminas and rare earth doped silica-aluminas. The BET surface area of the promoted alumina being preferably above 200 m^2/g, more preferably between 250 and 400 m^2/g.

Making the catalyst composition of the Invention

Generally, in making the catalyst composition of the invention an aqueous slurry comprising a pentasil-type zeolite and solid acidic cracking promoter is prepared and dried. Separate aqueous slurries of the pentasil-type zeolite and solid acidic cracking promoter may be prepared, mixed together and dried. The aqueous slurry may be spray dried to obtain catalyst particles having average lengths along their major axis of from about 20 microns to about 200 microns.

The catalyst composition of the invention may comprise one or more additional materials selected from the group consisting of particle binders, diluents, fillers and extenders. These may be added to the aqueous slurry comprising the pentasil-type zeolite and solid acidic cracking promoter.

Alternatively, the catalyst composition of the invention can be prepared by modifying a pentasil-type zeolite by ion exchange with ions selected from the group consisting of ions of alkaline earth metals, transition metals, rare earth metals, phosphorous, boron, aluminum, noble metals and combinations thereof, preparing an aqueous slurry of the solid acidic cracking promoter and other catalyst ingredients other than the modified pentasil-type zeolite, adding the modified pentasil-type zeolite to the slurry and shaping the slurry, the addition of the modified pentasil-type zeolite being carried out as a final step immediately prior to shaping. The addition of the modified pentasil-type zeolite may be carried out by mixing with the aqueous slurry until the slurry is substantially homogeneous. Shaping may be carried out by spray drying.

NH_4OH may be added to the slurry prior to the addition of the modified pentasil-type zeolite to raise the pH of the slurry. A pH buffer may be added to the slurry prior to the addition of the modified pentasil-type zeolite. The buffer may be selected from the group consisting of aluminum chlorohydrol, phosphate sol or gel, anionic clay, smectite and thermally or chemically modified clay. The thermally or chemically modified clay may be kaolin clay.

It is also possible to prepare the catalyst composition according to the invention by preparing an aqueous slurry comprising the solid acidic cracking promoter and precursors of the pentasil-type zeolite comprising silica, alumina, and seeds containing one or more metals from the group consisting of rare earth metals, alkaline earth metals and transition group metals, forming the aqueous slurry into shaped bodies and crystallizing the pentasil-type zeolite in situ in the shaped body.

Use of the catalyst of the invention

The refinery process in which use of the catalyst of the invention is contemplated may be any fluid catalytic cracking process designed to produce light olefins, having up to about 12 carbon atoms per molecule, such as FCC or

DCC. The process involves contacting a petroleum feedstock with an FCC catalyst composition of the invention at fluid catalytic cracking conditions, typically comprising a temperature from about 450-780°C, residence time from about 0.01 to 20 seconds, with and without added steam, and a catalyst-to-oil ratio from 1 to 100. This FCC catalyst composition may comprise about 5.0 to about 80 wt% of a mixture of the catalyst composition of the invention and a second fluidized catalytic cracking catalyst composition.

The catalyst composition according to the invention is very suitable for the production of olefins having up to about 12, preferably up to about 6 carbon atoms per molecule. Such a process involves contacting a petroleum feedstock at fluid catalytic cracking conditions with the catalyst composition according to the invention.

If it is desired to maintain the yield of olefins to at least about the level achieved by prior art compositions while maximizing the yield of gasoline and minimizing the yield of bottoms, a catalyst composition comprising a solid acidic cracking promoter comprising a rare earth and/or transition metal doped (pseudo) boehmite is preferably be used.

EXAMPLES

Comparative example 1

ZSM-5 (ex-Tricat) was mixed with H_3PO_4 solution at pH <3, dried, and calcined at 600°C for 1 hr. The resulting zeolite (15 wt-% P_2O_5) was milled and embedded into a slurry of a peptized (pseudo boehmite) alumina and clay. The slurry was mixed with high shear, dried, and calcined. The final composition was 15 wt-% ZSM-5, 65 wt-% Al_2O_3, and 10 wt-% clay. Absent from this blend was a solid acidic cracking promoter.

Example 2

Example 1 was repeated, but instead of 65 wt-% of (pseudo boehmite), alumina in the additive, the acidic cracking promoter contained 15 wt-% deeply stabilized, low sodium USY, 15 wt-% modified (pseudo boehmite) alumina, and 35 wt-% clay. The modified (pseudo boehmite) alumina was prepared by adding 975 g phosphoric acid and 5823 g $ReCl_3$ (Rare Earth) solution to a heel of H-water. Under stirring, 13700 g Natal (25 wt-% Al_2O_3) and 10172 g sulphuric acid was added at a fixed pH of 9.5 into the mixture. The slurry was aged at 100°C for 24 h, filtrated, washed, dried, and calcined.

The catalyst compositions according to Examples 1 and 2 were tested in a small scale fluidized bed reactor. The catalyst compositions according to the invention showed improved performance with respect to significant increase in gasoline and reduced bottoms yield, while simultaneously providing a high yield of light olefins.

A summary of catalyst properties and performance for the above Examples is given in the following Table.

Table of catalyst properties and performance

	Comp. Ex 1	Ex. 2
ABD	n.a.[2]	0.72
SA BET (m^2/g)	n.a.	231
Al_2O_3 (wt%)	n.a.	36.16
RE_2O_3 (wt%)	n.a.	6.79
P_2O_5 (wt%)	n.a.	4.67
Conversion (%)	76.0	78.3
Propylene yield (%)	11.1	13.3
Butylene yield (%)	9.4	10.8
Gasoline yield (%)	36.5	34.5
Bottoms yield (%)	9.1	7.9

[1]Small scale fluidized bed reactor at 540°C. Feed was a long residue with a CCR of 3.2

[2] not analyzed

As is clear from the Table, use of the composition of the invention results in a marked increase in the yield of olefins as compared to use of a conventional composition, while minimizing bottoms yield.

CLAIMS

1. A catalyst composition comprising a pentasil-type zeolite and one or more solid acidic cracking promoters.

2. The catalyst composition according to claim 1 comprising a filler, binder, diluent, and/or extender.

3. The catalyst composition according to claim 1 or 2 wherein said pentasil-type zeolite is selected from the group consisting of ITQ-type zeolite, beta zeolite, silicalite, and ZSM-type zeolite.

4. The catalyst composition according to any one of the preceding claims wherein said pentasil-type zeolite is doped with a compound comprising an ion selected from the group consisting of alkaline earth metal ions, transition metal ions, rare earth metal ions, phosphorous-containing ions, boron-containing ions, aluminum ions, noble metal ions, and combinations thereof.

5. The catalyst composition according to claim 1 wherein said pentasil-type zeolite comprises crystals having metals in tetrahedral coordination in said crystals selected from the group consisting of Al, As, B, Be, Co, Cr, Fe, Ga, Hf, In, Mg, Mn, Ni, P, Si, Ti, V, Zn, Zr, and mixtures thereof.

6. The catalyst composition according to any one of the preceding claims wherein said solid acidic cracking promoter is selected from the group consisting of alumina modified by incorporation of acid centers thereon or therein, acidic silica-alumina co-gels, acidic natural or synthetic clays, acidic titania, acidic zirconia, acidic titania-alumina, acidic zeolite materials and co-

gels of titania, alumina, zirconia, phosphates, borates, aluminophosphates, tungstates, molybdates and mixtures thereof.

7. The catalyst composition according to claim 6 wherein said acid centers are selected from the group consisting of halides, sulfates, nitrates, titanates, zirconates, phosphates, borates, silicates and mixtures thereof.

8. The catalyst composition according to any one of the preceding claims wherein said solid acidic cracking promoter comprises acidic silica-alumina, titania-alumina, titania/zirconia, alumina/zirconia or aluminum phosphate co-gels modified by the incorporation therein of metal ions or compounds selected from the group consisting of alkaline earth metals, transition metals, rare earth metals and mixtures thereof.

9. The catalyst composition according to any one of the preceding claims wherein the said solid acidic cracking promoter is a non-zeolitic solid acid having a BET surface area of at least 200 m^2/g.

10. The catalyst composition according to any one of the preceding claims wherein said solid acidic cracking promoter is a rare earth and/or silica doped alumina or a rare earth doped silica-alumina.

11. The catalyst composition according to claim 10 wherein the alumina is (pseudo)boehmite.

12. The catalyst composition according to any one of the preceding claims wherein the weight ratio of said pentasil-type zeolite to said solid acidic cracking promoter ranges from 0.03 to 9.0.

13. The catalyst composition according to any one of the preceding claims comprising from 5.0 wt% to 80 wt% of pentasil-type zeolite.

14. The catalyst composition according to any one of the preceding claims comprising from 5.0 wt% to 80 wt% of solid acidic cracking promoter.

15. A method of making the catalyst composition according to claim 4 wherein said pentasil-type zeolite is doped by (i) ion exchange of a pentasil-type zeolite with said ions, (ii) preparing the pentasil-type zeolite by using reactants doped with said ions, (iii) preparing the pentasil-type zeolite by using seeds doped with said ions, or (iv) preparing the pentasil-type zeolite by using a reaction mixture comprising said ions.

16. The method according to claim 15 involving the steps of ion exchanging the pentasil-type zeolite with ions selected from the group consisting of ions of alkaline earth metal ions, transition metal ions, rare earth metal ions, phosphorous-containing ions, boron-containing ions, aluminum ions, noble metal ions and combinations thereof, preparing an aqueous slurry of said acidic cracking promoter and other catalyst ingredients other than said ion exchanged pentasil-type zeolite, adding said ion exchanged pentasil-type zeolite to said slurry and shaping said slurry, said addition of said ion exchanged pentasil-type zeolite being carried out as a final step immediately prior to said shaping.

17. The method according to claim 16 wherein NH_4OH or a pH buffer is added to said slurry prior to the addition of said ion exchanged pentasil-type zeolite to raise the pH of said slurry.

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18. A method for preparing the catalyst composition according to any one of claims 1-14 wherein an aqueous slurry is prepared comprising said solid acidic cracking promoter and precursors of said pentasil-type zeolite comprising silica, alumina and seeds containing one or more metals from the group consisting of rare earth metals, alkaline earth metals and transition group metals, forming said aqueous slurry into shaped bodies and crystallizing said pentasil-type zeolite in situ in said shaped body.

19. A process for producing olefins having up to about 12 carbon atoms per molecule comprising contacting a petroleum feedstock at fluid catalytic cracking conditions with the catalyst composition according to any one of claims 1-14.

20. The process according to claim 19 wherein the yield of gasoline is maximized and the yield of bottoms minimized by using of a solid acidic cracking promoter comprising a rare earth and/or transition metal doped (pseudo) boehmite.