

149

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Señora Jefe de la
DIVISION DE NUEVAS CREACIONES
Superintendencia de Industria y Comercio
E. S. D.

Trámite : 011 Evento : 378 Actuación : 538

Referencia : Expediente No. 07099689
Asunto : Solicitud de patente para CATALIZADOR DE
REDUCCION DE AZUFRE PARA GASOLINA PARA
PROCESO DE CRAQUEO CATALÍTICO FLUIDO
Solicitante : W.R. GRACE & CO.-CONN.
Publicada en : La Gaceta No. 583 del 18 de diciembre de 2007

SOLICITUD EXAMEN DE PATENTABILIDAD

1. Yo, Emilio FERRERO, identificado como aparece al pie de mi firma, actuando como apoderado de la sociedad W.R. GRACE & CO.-CONN., atentamente solicito se efectúe el examen de patentabilidad de la solicitud en referencia presentada de acuerdo con las reglas del Capítulo I del PCT y según lo establecido en el artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina.

Para tal efecto presento junto con este escrito el recibo No. 08-42,183 del 27 de mayo de 2008 por valor \$420.000.00 que corresponde de la tasa legal fijada para el efecto.

2. Por lo anterior, comedidamente solicito se prosiga con el trámite de este asunto.

Señora Jefe,

EMILIO FERRERO
T.P.A. No. 31.929

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SCT\SCT\ID-127764\WPCL6032
No. M-2008-127764\SCT

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 07-99689

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **583** DE

FECHA **18 DE DICIEMBRE DE 2007** EL TÉRMINO HÁBIL SEÑALADO POR LA

LEY EXPIRA EL **14 DE MARZO DE 2008**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____ NO X

D1

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152

United States Patent [19]

Bertolacini et al.

[11] Patent Number: 4,542,116

[45] Date of Patent: Sep. 17, 1985

[54] CATALYST FOR REMOVING SULFUR
OXIDES FROM A GAS

[75] Inventors: Ralph J. Bertolacini, Naperville;
Eugene H. Hirschberg, Park Forest;
Frank S. Modica, Downers Grove,
all of Ill.

[73] Assignee: The Standard Oil Company, Chicago,
Ill.

[21] Appl. No.: 491,121

[22] Filed: May 3, 1983

Related U.S. Application Data

[62] Division of Ser. No. 363,269, Mar. 29, 1982, Pat. No.
4,405,443.

[51] Int. Cl.⁴ B01J 29/06

[52] U.S. Cl. 502/65; 502/73

[58] Field of Search 502/65, 73

[56] References Cited

U.S. PATENT DOCUMENTS

3,533,939 10/1970 Coonradt et al. 502/65 X
4,221,677 9/1980 Vasalos et al. 502/65
4,369,130 1/1983 Bertolacini et al. 502/65
4,399,059 8/1983 Chu 502/73

Primary Examiner—Carl F. Dees

Attorney, Agent, or Firm—Scott H. Brown; Fred E.
Hook

[57] ABSTRACT

Sulfur oxides are removed from a gas by an absorbent comprising at least one inorganic oxide selected from the group consisting of the oxides of aluminum, magnesium, zinc, titanium, and calcium in association with yttrium or yttrium combined with at least one free or combined rare earth metal selected from the group consisting of lanthanum, cerium, praseodymium, samarium, and dysprosium, wherein the ratio by weight of inorganic oxide or oxides to yttrium or yttrium combined with a rare earth metal or metals is from about 0.1 to about 30,000. Absorbed sulfur oxides are recovered as a sulfur-containing gas by contacting the spent absorbent with a hydrocarbon in the presence of a hydrocarbon cracking catalyst at a temperature from about 375° to about 900° C. The absorbent can be circulated through a fluidized catalytic cracking process together with the hydrocarbon cracking catalyst to reduce sulfur oxide emissions from the regeneration zone thereof.

15 Claims, 2 Drawing Figures

CATALYST FOR REMOVING SULFUR OXIDES FROM A GAS

This is a division, of application Ser. No. 363,269, 5
filed Mar. 29, 1982 now U.S. Pat. No. 4,405,443.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for reducing the 10
sulfur oxide content of a waste gas stream by using
absorbents which can be reactivated for further absorp-
tion of sulfur oxides by contact with a hydrocarbon in
the presence of a hydrocarbon cracking catalyst. More
particularly, this invention relates to a method for re- 15
ducing sulfur oxide emissions from the regenerator of a
fluidized catalytic cracking unit.

2. Setting of the Invention

A major industrial problem involves the development 20
of efficient methods for reducing the concentration of
air pollutants, such as sulfur oxides, in the waste gases
which result from the processing and combustion of
sulfur containing fuels. The discharge of these waste
gases into the atmosphere is environmentally undesir- 25
able at the sulfur oxide concentrations which are fre-
quently encountered. For example, such waste gases
result from combustion of sulfur containing fossil fuels
for the generation of heat and power, the regeneration
of catalysts employed in the refining of hydrocarbon 30
feedstocks which contain organic sulfur compounds, and
the operation of Claus-type sulfur recovery units.

Two basic approaches have been suggested for the 35
removal of sulfur oxides from a waste gas. One ap-
proach involves scrubbing the waste gas with an alka-
line material, such as lime or limestone, which reacts
chemically with the sulfur oxides to produce a nonvola-
tile waste product. This approach requires a large sup-
ply of the alkaline scrubbing material, and the resulting
reaction waste products may create a solid waste dis-
posal problem. The second basic approach uses sulfur 40
oxide absorbents which can be regenerated either ther-
mally or chemically. The process of this invention is
representative of this second approach.

One area of interest for reduction of sulfur oxides 45
from waste gas which uses the second basic approach is
cyclic, fluidized catalytic cracking of petroleum. This
process involves the cracking of a petroleum feedstock
in a reaction zone through contact with fluidized solid
particles of a cracking catalyst. The cracking catalyst
becomes substantially deactivated by nonvolatile coke
deposits and is separated from the reaction zone effluent 50
and stripped of volatile deposits in a stripping zone. The
stripped cracking catalyst particles are separated from
the stripping zone effluent, regenerated in a regenera-
tion zone by combustion of the coke with an oxygen
containing gas, and thereafter the regenerated catalyst 55
particles are returned to the reaction zone. If sulfur-con-
taining feedstocks are used in this process, the cracking
catalyst will become deactivated through the formation
of sulfur-containing deposits of coke. In conventional
processes, the combustion of this sulfur-containing coke 60
results in the release of substantial amounts of sulfur
oxides to the atmosphere.

Various methods have been used to reduce sulfur 65
oxide emissions by utilizing different types of reactants
with the cracking catalyst. A commonly utilized react-
ant is an alumina matrix combined with rare earth
metals. Many other metals have been tried; however, to

the best of our knowledge yttria (an oxide of yttrium)
has never been used as a reactant for this disclosed
purpose.

U.S. Pat. No. 3,835,031, to R. J. Bertolacini et al.
discloses a method for the reduction of the sulfur oxide
emissions through the use of a cracking catalyst com-
prising a zeolite in a silica-alumina matrix which has
from about 0.25 to about 5.0 weight percent of a Group
IIA metal or mixture of Group IIA metals distributed
over the surface of the matrix and present as an oxide or
oxides. The metal oxide or oxides react with sulfur
oxides in the regeneration zone to form nonvolatile
inorganic sulfur compounds. These nonvolatile inor-
ganic sulfur compounds are then converted to the metal
oxide or oxides and hydrogen sulfide upon exposure to
hydrocarbons and steam in the reaction and stripping
zones of the process unit. The resulting hydrogen sul-
fide is disposed of in equipment conventionally associ-
ated with a fluid catalytic cracking unit. Similarly, Bel-
gian Pat. No. 849,637 also is directed to a process
wherein a Group IIA metal or metals is circulated
through a cyclic fluidized catalytic cracking process in
order to reduce the sulfur oxide emissions resulting
from regeneration of deactivated catalyst. These pa-
tents do not suggest the use of yttrium or combining
yttrium with a rare earth metal for use as a reactant.

Belgian Pat. No. 849,636 and its counterpart, U.S.
patent application Ser. No. 748,556, disclose a process
similar to that set forth in U.S. Pat. No. 3,835,031,
which involves the removal of sulfur oxides from the
regeneration zone flue gas of a cyclic, fluidized, cata-
lytic cracking unit through the use of a zeolite-type
cracking catalyst in combination with a regenerable
metallic reactant. The reactant absorbs sulfur oxides in
the regeneration zone and releases the absorbed sulfur
oxides as hydrogen sulfide in the reaction and stripping
zones of the process unit. It is taught therein that a
suitable metallic reactant comprises one or more mem-
bers selected from the group consisting of sodium, scan-
dium, titanium, chromium, molybdenum, manganese,
cobalt, nickel, antimony, copper, zinc, cadmium, the
rare earth metals, and lead, all in free or combined form.
In addition, it is disclosed that the metallic reactant may
be supported by an amorphous cracking catalyst or a
solid which is substantially inert to the cracking reac-
tion. Silica, alumina and mixtures of silica and alumina
are mentioned as suitable supports. There is no specific
teaching, however, of the desirability of combining any
particular rare earth metals with inorganic oxides se-
lected from the group consisting of the oxides of
aluminum, magnesium, zinc, titanium and calcium. There
is no mention of the use of yttrium as a suitable reactant.
Further, the disclosure contains no suggestion that such
a combination would afford a synergistically enhanced
reduction of regenerator sulfur oxide emissions.

Belgian Pat. No. 849,635 and its counterpart, U.S.
patent application Ser. No. 748,555 are also directed to
a similar process to U.S. Pat. No. 3,835,031 and Belgian
Pat. No. 849,636, and teaches that an improved reduc-
tion of regeneration zone sulfur oxide emissions can be
achieved by combining a sulfur oxide absorbent with a
metallic promoter, including platinum and palladium.
The sulfur oxide absorbent comprises at least one free or
combined element which is selected from the group
consisting of sodium, magnesium, calcium, strontium,
barium, scandium, titanium, chromium, molybdenum,
manganese, cobalt, nickel, antimony, copper, zinc, cad-
mium, lead and the rare earth metals. Although the

the combination of yttrium or specific rare earth metals with specific metal oxides, such as alumina, could afford an improved sulfur oxide absorbent which can be regenerated by contact with a hydrocarbon in the presence of a hydrocarbon cracking catalyst.

SUMMARY OF THE INVENTION

This invention is directed to a process for removing sulfur oxides from a gas which comprises: (a) absorbing sulfur oxides from the gas with an absorbent which comprises at least one inorganic oxide selected from the group consisting of the oxides of aluminum, magnesium, zinc, titanium and calcium in association with yttrium at a temperature in the range from about 100° to about 900° C., wherein the ratio by weight of inorganic oxide or oxides to yttrium or yttrium with a metal is from about 1.0 to about 1,000, and (b) removing said absorbed sulfur oxides from the absorbent as a sulfur-containing gas, which comprises hydrogen sulfide, by contacting said absorbent with a hydrocarbon in the presence of a hydrocarbon cracking catalyst at a temperature in the range from about 375° to about 900° C.

In one embodiment, the present invention relates to a composition of matter prepared by the solid comprising: (a) impregnating a particulate solid cracking catalyst comprising from about 0.5 to about 50 weight percent of a crystalline aluminosilicate zeolite distributed throughout a matrix, consisting essentially of from about 40 to about 100 weight percent of alumina and from about 0 to about 60 weight percent of silica with yttrium, wherein the amount of the yttrium is sufficient to add from about 0.004 to about 10 weight percent, calculated as the metal or metals, to said catalyst particles; and (b) calcining said impregnated catalyst particles at a temperature between about 200° and about 820° C.

In a further embodiment, the present invention relates to a composition of matter comprising a particulate physical mixture of (a) a particulate solid cracking catalyst for cracking hydrocarbons comprising a crystalline aluminosilicate zeolite distributed throughout a matrix; and (b) a particulate solid, other than said cracking catalyst comprising at least one inorganic oxide selected from the group consisting of the oxides of aluminum, magnesium, zinc, titanium and calcium in association with yttrium, wherein the particulate solid other than cracking catalyst contains at least about 40 weight percent of the inorganic oxide or oxides, the ratio by weight of inorganic oxide or oxides to yttrium is from about 1.0 to about 1000, and said particulate solid other than cracking catalyst comprises from about 0.1 to about 50 weight percent of said particulate physical mixture.

It has been discovered that yttrium and the inorganic oxide or oxides of this invention act together in a synergistic manner to afford a more efficient absorption of sulfur oxides from a gas than is possible if they are used separately. Accordingly, it is an object of this invention to provide an improved composition of matter for use in absorbing sulfur oxides from a gas.

Another object of this invention is to provide an improved process for removing sulfur oxides from a gas.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation of the effect of various additives on SO₂ absorption; and

FIG. 2 is a graphical representation of the amount of SO₂ absorbed per unit of time for various concentrations of additives.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been discovered that an association of yttrium or a combination of yttrium with at least one free or combined rare earth metal selected from the group consisting of lanthanum, cerium, praseodymium, samarium and dysprosium, with at least one inorganic oxide selected from the group consisting of the oxides of aluminum, magnesium, zinc, titanium and calcium, is a highly efficient absorbent for sulfur oxides, which can be regenerated by contact with a hydrocarbon in the presence of a hydrocarbon cracking catalyst.

Yttrium is a metal commonly found in rare earth ores and has been occasionally referred to as a rare earth metal. Specifically, yttrium is not considered a rare earth metal itself. Yttrium has an atomic number of 39 and therefore does not lie in the rare earth grouping on the elemental periodic table, which have atomic numbers from 57 to 71. Yttrium is found in rare earth ores at a concentration of about 0.04% by weight. See Col. 7, line 60 to Col. 8, line 21 of U.S. Pat. No. 3,930,987. No reference is known which discloses the use of yttrium as an absorbent in a fluidized catalytic cracking process at the concentrations disclosed herein, i.e. the ratio by weight of inorganic oxide or oxides to oxide of yttrium is from about 1.0 to about 30,000. The other disclosure of yttrium in U.S. Pat. No. 3,930,987 does not mention a concentration of yttrium in a fluidized catalytic cracking process.

It has been found that the yttrium and the inorganic oxide or oxides act together in a synergistic manner to absorb sulfur oxides from a gas more efficiently than would be expected from their individual abilities to absorb sulfur oxides. Although the precise mechanism by which this synergism occurs is unclear, it is believed that the yttrium serves both to absorb the sulfur oxides and to assist in the transfer of sulfur oxides to the inorganic oxide. This transfer of sulfur oxides to the inorganic oxide may result from an ability of the yttrium to catalyze the conversion of sulfur dioxide to sulfur trioxide, which is more easily absorbed by the inorganic oxide. The yttrium does not, however, significantly enhance the combustion of carbon monoxide, which may also be present in the waste gas. Consequently, the process of this invention can be used to reduce sulfur oxide emissions from the regenerator of a fluidized, catalytic cracking unit wherein the regenerator vessel and/or associated process equipment, such as cyclones, cannot tolerate the increased temperatures which would result from an enhanced combustion of carbon monoxide. In addition, yttrium unlike metals such as platinum and palladium, does not significantly enhance the formation of nitrogen oxides in the regenerator of a fluidized catalytic cracking unit.

Catalytic cracking of heavy mineral oil fractions is one of the major refining operations employed in the conversion of crude oils to desirable fuel products such as high-octane gasoline fuels used in spark-ignited internal combustion engines. In fluidized, catalytic cracking processes, high molecular weight hydrocarbon liquids or vapors are contacted with hot, finely-divided, solid catalyst particles, either in a fluidized bed reactor or in an elongated riser reactor, and the catalyst-hydrocarbon mixture is maintained at an elevated temperature in

volatile products from the reaction and stripping zones and is separated and can be converted to elemental sulfur in facilities which are conventionally associated with a fluidized catalytic cracking unit.

In the practice of this invention, yttrium may be used alone or with at least one free or combined rare earth metal such as lanthanum, cerium, praseodymium, samarium and dysprosium. Lanthanum and cerium are thought to be the most effective rare earth metals for sulfur oxide absorption and cerium is generally more active than lanthanum.

The amount of yttrium utilized as an absorbent can be from about 1.0 wt % to about 15 wt % yttrium to inorganic oxide used as an absorbent, preferably, from about 6.0 wt % to about 12 wt %; and most preferably about 10 wt % to inorganic oxide. When the yttrium is used in combination with a rare earth oxide or oxides the following amounts of yttrium with rare earth oxide or oxides can be utilized: from about 0.5 wt % to about 8 wt % yttrium with from about 0.5 wt % to about 8 wt % of rare earth oxide or oxides to inorganic oxide used as an absorbent; preferably from about 3.0 wt % to about 6 wt % yttrium with from about 3.0 wt % to about 6 wt % rare earth oxide or oxides; and most preferably about 5 wt % yttrium with 5 wt % rare earth oxide or oxides.

In view of the similar chemical properties of the various rare earth elements, it is relatively difficult to separate them or their compounds from each other in pure form. For the practice of this invention, however, it is unnecessary to effect such a separation. A mixture of rare earth metals or compounds thereof of the type which is obtained from natural sources prior to any substantial separation of individual rare earth metals or compounds thereof can be used. Additionally, it is relatively simple to separate a cerium concentrate and a lanthanum concentrate from mixture of rare earth metals, and these concentrates contain a major portion of cerium and lanthanum respectively.

The oxides of yttrium and the rare earth metals are particularly effective in association with the inorganic oxide or oxides of this invention for absorbing sulfur oxides from a gas. Consequently, it is preferable to utilize yttrium and the rare earth metal or metals in the form of the oxide or oxides.

In the practice of this invention, at least one inorganic oxide is employed which is selected from the group consisting of the oxides of aluminum, magnesium, zinc, titanium, and calcium, and preferably at least one inorganic oxide selected from the group consisting of alumina and magnesium oxide is employed, and preferably alumina. Although the use of any form of alumina is contemplated for use in the practice of this invention, gamma-alumina and eta-alumina are preferred because of their usually large surface area.

A preferred embodiment of the invention involves the use of a mixture of inorganic oxides which comprises at least about 50 percent by weight of alumina. Mixtures of alumina with magnesium oxide and of alumina with zinc oxide are particularly suitable, wherein the weight ratio of alumina to magnesium oxide or zinc oxide is desirably from about 1.0 to about 500, and preferably from about 2.0 to about 100. In these embodiments, the desirable attrition and sulfur oxide releasing properties of alumina are combined with the excellent sulfur oxide absorption properties of the other metal oxides, particularly of magnesium oxide.

The inorganic oxides of this invention generally afford the best results when they have a large surface area. This surface area is desirably greater than about 10 square meters per gram, preferably greater than about 50 square meters per gram and ideally greater than about 100 square meters per gram. Similarly, yttrium and the rare earth metal or metals generally afford the best results when they have a large surface area exposed to the sulfur oxide containing gas as, for example, when the yttrium alone or yttrium with the rare earth metal or metals are deposited on a support having a large surface area. Such a support will have a surface area which is desirably in excess of about 10 square meters per gram, preferably greater than about 50 square meters per gram and ideally greater than about 100 square meters per gram. The larger surface areas are most desirable because of a more efficient contacting of the sulfur oxide containing gas with the solid.

The ratio of inorganic oxide or oxides to yttrium or yttrium with a rare earth metal or metals, calculated as the metal or metals, is desirably from about 0.1 to about 30,000, more desirably from about 1.0 to about 30,000, preferably from about 1.0 to about 1,000, and more preferably from about 2.0 to about 100, and ideally from about 3.0 to about 20. Decreasing the ratio of inorganic oxide or oxides to yttrium or yttrium with rare earth metal or metals generally affords an improved sulfur oxide absorption until a ratio of about 3.0 is reached. Smaller ratios than about 3.0 are not generally undesirable, but do not usually afford significant further improvement in sulfur oxide absorption properties. In addition, these smaller ratios require larger amounts of the metals which will generally be more expensive than the inorganic oxide or oxides.

Suitable hydrocarbon cracking catalysts for use in the practice of this invention include all high-activity solid catalysts which are stable under the required conditions. Suitable catalysts include those of the amorphous silica-alumina type having an alumina content of about 10 to about 60 weight percent. Catalysts of the silica-magnesia type are also suitable which have a magnesia content of about 20 weight percent. Preferred catalysts include those of the zeolite-type which comprise from about 0.5 to about 50 weight percent and preferably from about 1 to about 30 weight percent of a crystalline aluminosilicate component distributed throughout a porous matrix. Zeolite type cracking catalysts are preferred because of their thermal stability and high catalytic activity.

The crystalline aluminosilicate or zeolite component of the zeolite-type cracking catalyst can be of any type or combination of types, natural or synthetic, which is known to be useful in catalyzing the cracking of hydrocarbons. Suitable zeolites include both naturally occurring and synthetic aluminosilicate materials such as faujasite, chabazite, mordenite, Zeolite X (U.S. Pat. No. 2,882,244), Zeolite Y (U.S. Pat. No. 3,130,007), and ultrastable large-pore zeolites (U.S. Pat. Nos. 3,293,192 and 3,449,070). The crystalline aluminosilicates having a faujasite-type crystal structure are particularly suitable and include natural faujasite, Zeolite X and Zeolite Y. These zeolites are usually prepared or occur naturally in the sodium form. The presence of this sodium is undesirable, however, since the sodium zeolites have a low stability under hydrocarbon cracking conditions. Consequently, for use in this invention the sodium content of the zeolite is ordinarily reduced to the smallest possible value, generally less than about 1.0 weight

percent and preferably below about 0.3 weight percent through ion exchange with hydrogen ions, hydrogen-precursors such as ammonium ion, or polyvalent metal cations including calcium, magnesium, strontium, barium, yttrium and the rare earth metals such as cerium, lanthanum, neodymium and their mixtures. Suitable zeolites are able to maintain their pore structure under the high temperature conditions of catalyst manufacture, hydrocarbon processing and catalyst regeneration. These materials have a uniform pore structure with the cross-section diameter of the pores being in the range from about 4 to about 20 angstroms preferably from about 8 to about 15 angstroms.

The matrix of the zeolite-type cracking catalyst is a porous refractory material within which the zeolite component is dispersed. Suitable matrix materials can be either synthetic or naturally occurring and include, but are not limited to, silica, alumina, magnesia, boria, bauxite, titania, natural and treated clays, kieselguhr, diatomaceous earth, kaoline and mullite. Mixtures of two or more of these materials are also suitable. Particularly suitable matrix materials comprise mixtures of silica and alumina, mixtures of silica with alumina and magnesia and also mixtures of silica and alumina in combination with natural clays and clay-like materials. Mixtures of silica and alumina are preferred, however, and contain preferably from about 10 to about 65 weight percent of alumina mixed with from about 35 to about 90 weight percent of silica, and more preferably from about 25 to about 65 weight percent of alumina mixed with from about 35 to about 75 weight percent of silica.

In the practice of this invention, yttrium which is associated with one or more suitable inorganic oxides, are preferably used in a form which does not involve chemical incorporation within a zeolite.

In the practice of this invention, yttrium and inorganic oxide or oxides can be combined in any suitable manner and can be additionally combined with the hydrocarbon cracking catalyst. These materials, for example, can be combined and shaped into pellets or extrudates of any desired shape. In a highly preferred embodiment, the yttrium or yttrium with a rare earth metal or metals, the inorganic oxide or oxides, and the hydrocarbon cracking catalyst are employed in the form of particulate fluidizable solids. In this embodiment, the particles should be sufficiently strong that they are not subject to excessive attrition and degradation during fluidization. The average size of the solid particles will be desirably in the range from about 20 microns or less to about 150 microns, and preferably less than about 50 microns. The use of fluidized solids provides a highly efficient technique for contacting a gas with a solid or solids as is required in the practice of the process of this invention. Consequently, the use of fluidized solids affords a very efficient method of contacting the yttrium and inorganic oxide or oxides of this invention with a gas which contains sulfur oxides. Similarly, the use of fluidized solids also provides an efficient method of contacting the spent yttrium-inorganic oxide absorbent with a hydrocarbon in the presence of a cracking catalyst to remove the absorbed sulfur oxides.

When particulate solids are used in the practice of this invention, the particles of cracking catalyst can contain both yttrium and inorganic oxide or oxides. Alternatively, the particles of cracking catalyst can contain yttrium and be physically mixed with a separate particulate solid which comprises the inorganic oxide or ox-

ides. As a further alternative, the particles of cracking catalyst can contain the inorganic oxide or oxides and be physically mixed with a separate particulate solid which comprises yttrium. In addition, a physical mixture of different particulate solids can also be employed wherein one particulate solid comprises the cracking catalyst, yttrium comprise the second particulate solid, and the inorganic oxide or oxides comprise the third particulate solid. It will, of course, be appreciated that combinations of these alternatives are also possible.

The inorganic oxide or oxides of this invention can comprise a portion of a cracking catalyst as, for example, in the case of a silica-alumina or silica-magnesia catalyst. Also, the inorganic oxide or oxides of this invention can comprise at least a portion of the matrix of a zeolite-type cracking catalyst. A particularly preferred embodiment of this invention comprises the use of alumina as the inorganic oxide, which is provided in the form of a zeolite-type cracking catalyst having alumina in its matrix.

The use of a zeolite-type cracking catalyst having a high alumina matrix, for example in excess of about 40 weight percent, provides a highly convenient manner in which to provide the inorganic oxide of this invention. As the alumina content of the matrix increases, the ability of the cracking catalyst to absorb sulfur oxides in accordance with this invention also increases.

The inorganic oxide or oxides and yttrium of this invention can be in the form of a fluidizable powder which is admixed with a particulate cracking catalyst. Illustrative of such powders are alumina, magnesia, titania, zinc oxide, calcium oxide, cerium oxide, lanthanum oxide and mixed rare earth oxides comprising cerium and/or lanthanum.

As described above, yttrium as well as the inorganic oxide or oxides can be incorporated into or deposited onto a suitable support. Suitable supports include, but are not limited to, amorphous cracking catalysts, zeolite-type cracking catalysts, silica, alumina, mixtures of silica and alumina, magnesia, mixtures of silica and magnesia, mixtures of alumina and magnesia, mixtures of alumina and magnesia with silica, titania, zinc oxide, calcium oxide, natural and treated clays, kieselguhr, diatomaceous earth, kaolin and mullite. Such support preferably comprises at least one of the inorganic oxides of this invention. Suitable supports for the inorganic oxide or oxides can be silica, natural and treated clays, kieselguhr, diatomaceous earth, kaolin and mullite. Also an inorganic oxide can be a support for one or more other inorganic oxides. Desirably, the support is porous and has a surface area, of at least about 10 square meters per gram, preferably at least about 50, and most preferably at least about 100 square meters per gram. Large surface areas are desirable because of a more efficient contacting of the sulfur oxide containing gas with the solid.

Yttrium and/or inorganic oxide or oxides of this invention can be combined with a support either during or after preparation of the support. One method consists of impregnating a suitable support with an aqueous or organic solution or dispersion of a compound or compounds of yttrium and/or metal or metals of the inorganic oxide or oxides. The impregnation can be carried out in any manner which will not destroy the structure of the support. After drying, the composite can be calcined to afford the supported rare earth metal or metals and/or inorganic oxide or oxides of the invention. Preferably, nitrates, carbonates and salts of organic acids

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCIÓN DE NUEVAS CREACIONES

157

2020
Bogotá, D.C.

Abogado
EMILIO FERRERO

ASUNTO	Radicación	07 099 689
	Trámite	011
	Evento	378
	Actuación	519
	Oficio	07081
	Folios	010

Patente de Invención	☒	
Vía PCT (fase nacional)	☒	Cap. I ☒

No. Solicitud Internacional PCT/US2006/006795

Fecha de Presentación Internacional 24/febrero/2006

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Folios 72 a 122	como se radicó inicialmente.
Reivindicaciones:	Folios 123 a 129	como se radicó inicialmente
Dibujos:	Folios 131 a 140	como se radicó inicialmente
Oposiciones:	No se presentaron.	

Respuesta del solicitante:

Prioridad: US 60 656 461 de febrero 25 de 2005

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque:
Esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486).
Y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

Título de la solicitud: "Catalizador de azufre para gasolina para proceso de craqueo catalítico fluido"

El problema planteado en esta solicitud es proveer un catalizador capaz de reducir la cantidad de azufre de hidrocarburos craqueados, además que sea adecuado para el

uso en procesos de craqueo catalítico fluidizado donde sea capaz de reducir significativamente el contenido de azufre principalmente de las fracciones de gasolina ligera y pesada, y que su actividad permanezca por un amplio período de tiempo.

para resolver este problema técnico la solicitud en estudio proporciona una composición catalítica de craqueo mejorada que comprende zeolita e itrio y preferiblemente zinc presentes como cationes, la composición es particularmente adecuada para el uso en un proceso de craqueo catalítico fluidizado; además se suministra un nuevo método para reducir el contenido de azufre (incluyendo azufre LCO) de una fracción de petróleo catalíticamente craqueada empleando la presente composición de catalizador de craqueo, y un nuevo proceso de craqueo catalítico fluido.

El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): B01J 029/006

4. De la Solicitud de Patente

Reivindicaciones (Art. 30 D 486, Art. 22 PCT)

Las reivindicaciones 2, 5, 6, 14, 21, 25 – 27 y 34 – 36 no son claras porque:

El término “aproximadamente” es impreciso por lo cual no permite distinguir la invención del estado de la técnica. Se sugiere sustituirlo por un término preciso o un rango concreto.

La reivindicación 15 presenta dependencia incorrecta. Se requiere hacer la corrección. Se sugiere hacerla dependiente de la reivindicación 1.

La reivindicación 16 presenta dependencia incorrecta. Se requiere hacer la corrección. Se sugiere hacerla dependiente de la reivindicación 15.

La reivindicación 22 presenta dependencia incorrecta. Se requiere hacer la corrección. Se sugiere hacerla dependiente de la reivindicación 6.

La reivindicación 32 presenta dependencia incorrecta. Se requiere hacer la corrección. Se sugiere hacerla dependiente de la reivindicación 31.

La reivindicación 41 presenta dependencia incorrecta. Se requiere hacer la corrección. Se sugiere hacerla dependiente de la reivindicación 40.

La reivindicación 43 presenta dependencia incorrecta. Se requiere hacer la corrección. Se sugiere hacerla dependiente de la reivindicación 42.

La reivindicación 33 no es clara porque:

La redacción no hace fácil comprender el objeto que busca protección.

Las reivindicaciones 33 – 43 no son claras porque:

La traducción al castellano no es la más adecuada. Donde dice: “...catalizador para reducción de azufre de producto...” se sugiere cambiar por “...producto de catalizador para reducción de azufre...” o solo “...catalizador para reducción de azufre...” para facilitar la comprensión de cada reivindicación.

Se requiere corregir la traducción al castellano de los nombres de los elementos químicos nombrados en las reivindicaciones 9, 10, 30 y 39.

Se requiere al Solicitante hacer las aclaraciones necesarias.

5. Unidad de invención (Art 25 D 486)

La solicitud presenta falta de unidad *a posteriori* (numeral 8.3, Capítulo III: Examen de fondo, Manual Andino de Patentes, 2003) lo cual se evidencio por lo siguiente:

La solicitud presenta las siguientes reivindicaciones independientes:

Reivindicación 1: relacionada con una composición de catalizador.

Reivindicación 24: relacionada con método para reducir el contenido de azufre de una fracción de petróleo catalíticamente craqueada. Y

Reivindicación 33: relacionada con proceso de craqueo catalítico fluido.

El único concepto inventivo que se puede considerar relaciona las tres anteriores reivindicaciones es el catalizador que comprende zeolita, itrio, y por lo menos un elemento seleccionado del grupo que consiste de zinc, magnesio y manganeso, en donde el itrio y el elemento están presentes como cationes (parte caracterizante de la reivindicación 1). Y como se examina en el numeral 7 de éste documento no cumple con los requisitos de novedad; entonces, "las características técnicas especiales de cada "alternativa" ya no pueden estar unidas por ese concepto único" (numeral 8.3, Capítulo III: Examen de fondo, Manual Andino de Patentes, 2003).

Por lo tanto se requiere limitar la aplicación a un solo grupo inventivo o grupos donde se relacione otro concepto inventivo único o presentar las Solicitudes Divisionales que el solicitante considere necesarias.

Se sugieren los siguientes Grupos Inventivos:

Grupo 1: Reivindicaciones 1 – 23, relacionado con la composición del catalizador.

Grupo 2: Reivindicaciones 24 – 32, relacionado con el método para reducir el contenido de azufre de una fracción de petróleo catalíticamente craqueada.

Grupo 3: Reivindicaciones 33 – 43, relacionado con proceso de craqueo catalítico fluido.

6. Determinación del Estado de la Técnica

El Estado de la Técnica se determinó con base en la:

Fecha de Presentación de la Solicitud de Prioridad: febrero 25 de 2005

Y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Item	Documento	Título	Fecha de Publicación
D1	US4542116	Catalyst for removing sulfur oxides from a gas	17/septiembre/1985

D1 divulga (columna 1, renglones 10 - 17) un proceso para reducir el contenido de óxido de azufre de una corriente de gas residual por el uso de absorbentes los cuáles pueden ser reactivados para seguir absorbiendo óxidos de azufre por el

contacto de un hidrocarburo en presencia de un catalizador de craqueo de hidrocarburos; más específicamente relata método para reducir las emisiones de óxido de azufre del regenerador de una unidad de craqueo catalítico fluidizado (FCCU, por sus siglas en Inglés).

7. Examen de Patentabilidad (Art 14 D486)

Este examen solo se realiza al primer Grupo Inventivo, anteriormente presentado.

Novedad (Art 16 D486)

La reivindicación 1 se refiere a una composición de catalizador **que comprende** zeolita, itrio, y por lo menos un elemento seleccionado del grupo que consiste de zinc, magnesio y manganeso, en donde el itrio y el elemento están presentes como cationes.

Comparación de las características técnicas **esenciales**, con las del estado de la técnica:

Características esenciales	D1
PRODUCTO: Composición de catalizador que comprende:	
- zeolita	√
- itrio (catión)	√
- zinc o magnesio o manganeso (catión)	√

Las características técnicas **esenciales** de la reivindicación 1 habían sido divulgadas previamente en el documento del estado de la técnica (D1), en el cuál se revela una composición catalítica que comprende un catalizador de craqueo basado preferiblemente en una zeolita Y, la cuál es una zeolita de naturaleza sódica, y para la invención referida (proceso para reducción de óxidos de azufre en efluentes gaseosos) el contenido de sodio es reducido por medio de intercambio iónico, usando precursores de hidrógeno como cationes de metales polivalentes incluyendo itrio y magnesio y metales de tierras raras como cerio y lantano y sus mezclas (D1: columna 10/renglón 59 – columna 11/renglón 6), además de lo anterior el catalizador puede incluir un sólido particulado que comprende un óxido inorgánico seleccionado de aluminio, magnesio, zinc, titanio y calcio en mezcla con itrio (D1: columna 5/renglones 38 – 47), por lo tanto dicha reivindicación no se considera nueva.

Aplicación industrial (Art 19 D 486)

El grupo de reivindicaciones analizadas cumplen con el requisito de Aplicación Industrial, ya que la materia reivindicada es susceptible de ser realizada o usada en la industria.

8. Conclusión

Los requisitos de Patentabilidad del Grupo Inventivo examinado están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US4542116	1 - 23	Novedad

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de 60 días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar