RARE EARTH BINDER-CONTAINING ADDITIVES AND CATALYSTS

This application is a continuation-in-part of U.S. Patent Application Serial No. 08/315,320 filed September 29, 1994, now _____.

Background of the Invention

There are many well known cracking catalysts and additive compositions which are useful in converting metals-containing hydrocarbon feedstocks into valuable products such as gasoline and diesel fuel.

When zeolite-containing cracking catalysts are used to process feedstocks which contain metals such as vanadium, the metals are deposited on the catalyst in amounts that eventually cause loss of activity and/or increased production of undesirable products such as hydrogen and coke.

The prior art discloses various methods for improving the catalytic cracking activity and selectivity of catalytic cracking catalysts in the presence of V where a rare earth component is added to the catalyst.

U.S. Pat. 3,930,987 describes a process wherein cracking catalyst composite particles (comprising a zeolite in a matrix) are impregnated with a solution of rare earth salts. Various soluble rare earth salts may be used to prepare the catalysts.

U.S. Pat. 4,515,683 discloses a method for passivating vanadium on catalytic cracking catalysts wherein lanthanum is nonionically precipitated on the catalyst prior to ordinary use. In a preferred embodiment, lanthanum is precipitated by the addition of ammonium hydroxide or oxalic acid to a catalyst which has been previously impregnated with a rare-earth chloride solution.

U.S. Pat. 4,921,824 discloses a catalytic cracking catalyst which contains separate and discrete particles of lanthanum oxide. The lanthanum oxide particles are added as separate particles along with the catalyst particles during the cracking process. The lanthanum oxide additive may include an inert matrix such as clay, silica and/or a metal oxide.

U.S. Pats. 5,194,413 and 5,248,642 disclose cracking catalysts and additives which contain an inorganic rare earth oxide and/or oxychloride dispersed as discrete particles in clay/alumina and/or reacted metakaolin matrix. The catalysts are particularly active for the cracking of metal-containing hydrocarbon feedstocks.

While these compositions have been effective in dealing with the presence of vanadium, there remains a continued desire for improved catalyst and additive compositions which provide greater activity in the presence of vanadium. Further, there is a desire for greater flexibility for incorporation of a rare earth component into catalyst and/or additive particles.

Summary of the Invention

The invention provides improved cracking catalyst and additive compositions that are highly effective for controlling the adverse effects of metals such as vanadium wherein those compositions are characterized by the presence of a rare earth compound binder material.

In one aspect, the invention encompasses compositions especially useful in catalytic cracking wherein zeolitic cracking catalyst particles and/or other particles are bound by rare earth compound binder. The rare earth compounds contained in the binder are preferably selected from the group consisting of oxides, oxychlorides, oxycarbonates, and mixtures thereof.

In another aspect, the invention encompasses the use of a rare earth compound binder in combination with an auxiliary binder material. The auxiliary binder is preferably selected from the group consisting of peptized alumina and colloidal silica.

In another aspect, the invention encompasses the compositions containing high surface area filler particles in combination with a rare earth compound binder material. Preferred high surface area particles are silica xerogels and silica hydrogels.

The invention also encompasses methods for preparing compositions containing the rare earth compound binder materials of the invention wherein a rare earth acid sol or rare earth salt solution is combined with the desired particulate

material and is subsequently converted into the desired rare earth compound material. The invention further encompasses improved methods for catalytic cracking of hydrocarbons using the compositions of the invention.

These and other aspects of the invention are described in further detail below.

Brief Description of Drawings

Figures 1 to 4 are graphic plots of catalytic cracking data which illustrate the performance of compositions of the invention.

Figure 5 is a schematic cross section of a rare earth compound binder-containing composition contemplated by the invention.

Detailed Description of the Invention

The invention encompasses compositions characterized by the presence of a rare earth compound binder material and one or more particulate materials bound by the rare earth compound binder. The compositions of the invention are especially useful in catalytic cracking processes where a hydrocarbon feedstock to be cracked contains significant amounts of vanadium, however the compositions may be used in other processes.

The rare earth compound binder material preferably comprises rare earth compound(s) selected from the group consisting of oxides, oxychlorides, oxycarbonates and mixtures thereof. Most preferably, the rare earth compound material consists essentially of the these rare earth compounds. The rare earth metal in the compound(s) may be any rare earth metal or mixture thereof. Preferably, the rare earth metal is selected from the group consisting of lanthanum, neodymium, cerium and mixtures thereof. Most preferably, the rare earth metal consists essentially of lanthanum. Preferably, the rare earth compound phase is derived from a rare earth acid sol, however the rare earth compound phase may also be derived from a rare earth compound solution (e.g. a rare earth salt such as rare earth chloride). Most preferably,

the rare earth compound phase consists essentially of lanthanum compounds derived from a rare earth acid sol.

If desired, an auxiliary binder may be used in combination with the rare earth binder. The auxiliary binder may be any sol or colloidal component which acts with the rare earth compound binder to improve the attrition resistance of the metals passivation component. Preferred auxiliary binders are selected from the group consisting of silica sol (colloidal silica) and alumina sol (preferably peptized alumina). Preferably, any auxiliary binder present is at a level of 50 wt.% (oxide basis) or less based on the total weight of rare earth binder and auxiliary binder. More preferably, the auxiliary binder forms about 40 wt.% of the total binder weight (most preferably, about 1/3 or less of the total binder weight).

Figure 5 provides a schematic illustration of one possible composition of the invention. This illustration is presented to clarify the discussion below regarding various possible components of the compositions. It should be noted that the relative sizes of the various components depicted in Figure 5 is not to scale. Further, the particles have been depicted as spherical for ease of illustration. The particles may be irregularly shaped.

The binder material **2** may be homogeneous or heterogeneous. For example, the binder **2** may contain a fine particulate material **4** in addition to a continuous rare earth compound phase **6** so long as that fine particulate **4** does not interfere with the ability of the binder **2** to bind the desired (larger) particulate material **8** which is also present in the overall composition **10**. As noted above, the binder **2** may be a combination of rare earth compound binder and auxiliary binder(s). If any fine particulate material **4** is present in the binder **2**, preferably that material is itself a rare earth compound or an oxide from which the auxiliary binder is derived. Most preferably, the fine particulate material **4** comprises a rare earth compound selected from the group consisting of oxides, oxychlorides, oxycarbonates and mixtures thereof. Other compounds (in addition to any auxiliary binder) may be present in the rare earth compound phase **6** in minor amounts as long as they do not adversely affect the

performance of the overall composition with respect to cracking of metal-containing feedstocks.

The particulate phase may include particles of any material which does not adversely affect the performance of the rare earth compound phase with respect to V and/or Ni nor the performance of the overall catalytic cracking process.

The compositions of the invention can be used in at least the following modes:

a. as an additive particle added to catalytic cracking reactor separately or as a physical admixture with cracking catalyst particles,

b. as an additive incorporated into a cracking catalyst particle, or

c. as a catalytic cracking catalyst particle having a rare earth compound binder phase.

Where the composition of the invention is used as a separate additive to the reactor (mode a. above) or as an additive incorporated into a cracking catalyst particle (mode b. above), the particulate bound in the composition preferably comprises a non-zeolitic material selected from the group consisting of clays (such as kaolin), alumina, silica, and other non-zeolitic filler materials. Where peptized alumina is used as an auxiliary binder, preferably at least some of the filler particles are alumina particles. The filler particles may have some functionality beyond simply adding less expensive bulk to the composition. In some cases, if greater metal passivation is desired, the bound particles may comprise or consist essentially of additional rare earth compound particles adapted to provide additional metal passivation. High surface area filler particles may be incorporated into the compositions of the invention to improve the metals passivation performance. Preferred high surface area filler particles are silica xerogels and hydrogels, however any suitable high surface area particles may be used. If desired, mixtures of diverse particles can be used as the bound particulate phase.

Where the composition of the invention is itself used as a particulate cracking catalyst (mode c. above), the particulate material (bound by the rare earth compound material) preferably comprises a zeolitic cracking catalyst (e.g. a zeolite Y). Virtually any known cracking catalyst may be incorporated into the composition of the

invention. If desired, other particulate materials can also be incorporated into the composition along with the zeolitic cracking catalyst.

Where the composition of the invention itself is used as an additive or as a cracking catalyst, the total amount of binder phase (rare earth and any auxiliary binder) in the composition is preferably about 10-75 wt.% based on the total dry weight of the composition. Where the composition is used as an additive (mode a. or b. above), the composition more preferably contains about 20-60 wt.% of the binder phase. Where the composition is itself used as a cracking catalyst (mode c. above), the composition more preferably contains about 10-25 wt.% of the binder phase. The balance of the composition would be particulate components bound by the binder phase.

The relative proportions of the bound particulate components may be varied depending on the intended use of the composition (e.g. mode a. vs. mode c.). In general, on a parts by dry weight basis, the bound particulate components preferably comprise about 0-90 parts by wt. clay, more preferably about 40 to 80 parts; about 0-80 parts alumina, more preferably about 20 to 70 parts; and 0-50 parts by weight zeolite (molecular sieve), more preferably about 0 to 20 parts. Where the composition is itself used as a cracking catalyst, the amount and type of zeolite present in the composition should be such that the resulting composition is an effective cracking catalyst.

As noted above (regarding mode b.), the rare earth-containing compositions of the invention may be incorporated into commercial zeolite-containing fluid cracking catalysts (FCC) particles. Examples of commercial cracking catalysts are OCTACAT®, ORION®, SUPER-D®, DA® and XP® catalysts manufactured and sold by the Davison Chemical Division of W. R. Grace & Co.-Conn. FCC catalysts typically comprise a zeolite (molecular sieve) such as type X, Y, ultrastable Y (USY), rare earth-exchanged Y (REY), Beta, and/or ZSM-5 dispersed in silica, alumina or silica-alumina clay matrix. Preferred zeolites are disclosed in U.S. Pat. 3,402,996 (CREX and CREY), U.S. Pat. 3,293,192 and 3,449,070 (USY), U.S. Pats. 3,595,611, 3,607,043, 3,957,623 (PCY) and U.S. Pat. 3,676,368 (REHY). The FCC catalyst

may be prepared in accordance with any known method such as those disclosed in U.S. Pats. 3,957,689, 4,499,197, 4,542,118 and 4,458,023 or Canadian Pat. 967,136. The disclosures of these various patents are incorporated herein by reference. The rare earth binder-containing compositions preferably form about 5 to 25 wt.% of the FCC particles, more preferably about 5 to 15 wt.%. Similar proportions of the compositions of the invention are also preferred where the compositions of the invention are used as separate particulate admixtures in conjunction with FCC particles.

While the compositions of the invention are not limited to any specific method of manufacture, processes using rare earth salt solutions or acid sols of rare earth metal compounds are preferred. A discussion of rare earth sols can be found in U.S. Pat. 3,024,199 the disclosure of which is incorporated herein by reference. Preferably, the rare earth binder-containing compositions of the invention are obtained by a method comprising:

(a) mixing a rare earth compound sol or rare earth salt solution with the particles to be bound to form a mixture,

(b) forming the resulting mixture into particles, and

(c) calcining the mixture particles to obtain particles which themselves comprise the particles added in step (a) bound by a rare earth compound phase.

The rare earth compound sol or salt solution may be formed by any conventional method.

Where a rare earth sol is used, it is preferably obtained by peptizing a slurry of rare earth compound material with a monobasic acid. In the peptizing step, the monobasic acid(s) is preferably added to an aqueous slurry of the rare earth compound material to be peptized. The peptizing reaction is then allowed to occur. If desired, the slurry can be heated to accelerate the peptization. Preferably, the peptization is conducted at about 20°-90°C. The peptization can be carried out for whatever time is necessary to form a sol which is capable of forming the desired rare earth binder phase.

In some instances, it may not be necessary to completely react the starting rare earth material with the acid providing that the above mentioned condition is met by the resulting sol. Preferably, the peptization is allowed to proceed for about 5 minutes to 2 hours.

The solids content of the initial slurry is preferably about 5-20 wt.%. The amount of the acid used is preferably an amount which is sufficient to peptize all the initial rare earth compound material. The mole ratio of acid to rare earth compound in the initial slurry preferably ranges from about 1-4. If desired, agitation may be employed to facilitate forming the initial slurry and/or the resulting sol. It may be possible in some instances to add expedients such as dispersants to the initial slurry or the rare earth sol. Where peptized alumina is used as an auxiliary binder, preferably it is formed by adding alumina to the rare earth compound-monobasic acid mixture wherein an excess of monobasic acid has been used (i.e., beyond that needed to simply peptize the rare earth compound.) The peptized alumina may be partially or fully peptized.

For peptization, the initial rare earth compound material may contain any rare earth compounds capable of forming a sol and of forming the desired rare earth compounds in the calcined end product. Preferably, the rare earth compounds to be peptized are selected from the group consisting of oxides, carbonates, hydroxides, oxychlorides and mixtures thereof. Preferably, the rare earth elements in the compounds to be peptized are selected from the group consisting of lanthanum, neodymium, cerium and mixtures thereof. Preferably, the rare earth compounds consist essentially of lanthanum compounds.

For peptization, the monobasic acid may be any organic or inorganic acid capable of peptizing the initial rare earth compound material. The monobasic acid may be selected to alter the composition of the rare earth compound phase obtained after calcination (compared to the composition of the initial rare earth material) or may be selected such that little or no difference in the make up of the rare earth compounds occurs between the initial rare earth compound material to be peptized and the rare

earth compound phase after calcination. For example, the use of hydrochloric acid will typically result in the formation of rare earth oxychloride in the calcined product whereas the use of nitric acid will typically result in the formation of rare earth oxide in the calcined product. Preferably, the monobasic acid is selected from the group consisting of formic acid, acetic acid, hydrochloric acid, and nitric acid. Formic acid is generally preferred.

Where a rare earth salt solution is used, it is preferably formed by simply dissolving the desired rare earth salt(s) in water. The concentration of salt in the solution is preferably such that the mixture resulting from step (a) can be spray dried to yield a composition with the desired amount of rare earth binder. Preferred rare earth salts are selected from the group consisting of rare earth chlorides and nitrates.

In mixing step (a), the rare earth sol (or solution) is combined with a particulate material. The mixing may be performed by any conventional means. Preferably, the sol (or solution) and particulate material are subjected to milling. The consistency of the resulting mixture is preferably such that the mixture can be formed into particles by spray drying.

The amount of sol (or solution) in the mixture should be sufficient enough so that the rare earth phase will act as a binder for the particulate material in the calcined particle. Preferably, the rare earth sol (or solution) and particulate material are combined such that the resulting mixture contains about 15 to 75 wt.% of the rare earth compounds (measured as the rare earth compounds present in the initial rare earth compound material) based on the total weight of the rare earth compounds and the particulate material.

Where an auxiliary binder is used, it is preferably added to the mixture before the mixture is formed into particles. As noted above in the case of peptized alumina and rare earth sol, the auxiliary binder may be formed by peptizing in the same mixture as the rare earth sol by subsequent addition in the presence of excess monobasic acid.

The mixture from step (a) may be formed into particles by any known method. Preferably, the mixture is formed into particles by spray drying. For spray drying, the

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mixture preferably has a solids content of about 10 to 30 weight percent. If necessary, the solids content of the sol-particle mixture can be altered by addition or removal of liquid. The spray drying is preferably conducted at a temperature of about 160 to 190°C to obtain particles having a size range of 10 to 150 microns (mm).

The spray dried particles are then calcined. The calcining is preferably performed at a temperature of 400 to 800°C for about 1 hour. During the calcination, the rare earth compounds are reacted to form the desired rare earth phase composition and to transform the spray dried particles into dense, attrition-resistant particles containing a particulate phase bound by a rare earth compound phase. If desired, the calcining conditions can be used to influence the composition of the resulting rare earth phase. For example, where an oxide or mixture of oxide and other compound is desired, the calcination can be conducted in the presence of steam to promote formation of rare earth oxide.

The calcined particles preferably possess the following catalytic and physical properties:

(1) a microactivity of 10 to 80 as determined by ASTM 3907;

(2) a Davison (attrition) Index (DI) of 1 to 30;

(3) a density of 0.6 to 1.0 g/cc;

(4) a surface area of 20 to 200 m^2/g.

The Davison Index (DI) is determined as follows:

A sample of catalyst is analyzed to determine the 0 to 20 micron size content. The sample is then subjected to a 1 hour test in a Fluid Catalyst Attrition Apparatus using a hardened steel jet cup having a precision bored orifice. An air flow of 21 liters a minute is used. The Davison Index is calculated as follows:

$$\text{Davison Index} = \frac{\text{wt. \% 0-20 micron material formed during test}}{\text{wt. original 20 + micron fraction}}$$

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The compositions are preferably used in FCC processes conducted at cracking reaction temperatures of 500 to 600°C and regeneration temperatures of 600 to 850°C using hydrocarbon feedstocks that may contain up to 100 ppm or more of V and Ni. The presence of the compositions of the invention during the FCC process passivates the adverse effects of metals such as vanadium and decreases the formation of hydrogen and coke. It is believed that use of the compositions of the invention will permit the successful use of FCC regeneration catalysts that contain as much as 10,000 to 20,000 ppm V.

The following examples are given to further illustrate specific embodiments of the invention. The invention is not limited to the specific details of the examples.

Example 1

Preparation of Peptized La_2O_3

Samples of peptized La_2O_3 acid sol were prepared by reacting lanthana (La_2O_3 sold by Johnson Mathy-Alpha Div. under the catalog number 55334-Z3) with formic acid (HCOOH) as follows:

La_2O_3 was first slurried in water at about 25°C. The solid content of the slurry was from about 8-15 percent. Samples of the La_2O_3 slurry were combined with various amounts of formic acid while the slurry was intensely mixed. After the addition of the formic acid, the mixing was continued for about 10 minutes. The resulting sols possessed a $HC00H/La_2O_3$ mole ratio of 1.0, 1.5, 2.0 and 3.0 respectively.

Example 2

Preparation of La oxycarbonate/Clay Composition

The sols of Example 1 were each combined with kaolin particles as follows:

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25 wt.% La_2O_3 and 75 wt.% kaolin (Samples 1, 2 & 3)

50 wt.% La_2O_3 and 50 wt.% kaolin (Samples 4, 5 & 6)

The solids content (total of La compound (calculated on an oxide basis) and kaolin) of the resulting mixtures ranged from 14-25 wt.% as indicated in Table I. The mixtures were milled, spray dried, and calcined in a muffle furnace for 1 hour at 593°C (1100°F).

The chemical and physical properties of the additive samples is set forth in Table I.

TABLE I

Composition (wt.%)	**25% La_2O_3-75% Clay**			**50% La_2O_3-50% Clay**		
Sample No.	**1**	**2**	**3**	**4**	**5**	**6**
Peptized La_2O_3 Composition						
$HCOOH/La_2O_3$ (moles)	1.5	2.0	3.0	1.0	2.0	3.0
$HCOOH/La_2O_3$ (wt.)	0.21	0.28	0.42	0.14	0.28	0.42
Spray Dryer Feed Solids wt. %	24.7	24.6	18.6	20.7	15.5	14.3
Heat Treatment: 1 HR. at 593°C						
La_2O_3 wt.%	22.67	23.27	24.66	56.53	45.44	47.31
H_2O PV cc/g	0.75	0.54	0.46	0.40	0.38	0.36
APS mm	60	62	52	57	49	50
SA, m^2/g	31	26	26	28	25	26
ABD g/cc	0.47	0.62	0.63	0.79	0.80	0.77
DI	11	17	11	20	13	25

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Example 3

Preparation of Vanadium-Containing Additive/FCC Mixtures

In order to test the ability of the compositions of the invention to combat the adverse effects of vanadium, two samples of FCC cracking catalysts were prepared by blending a commercial zeolite-containing cracking catalyst (ORION® 822 sold by Grace Davison) with 10 weight percent of Samples No. 3 and 5 of Example 2 (Blends B and C in Table II). An additional sample (Blend A) was prepared without the composition of the invention as a comparison sample (containing only the ORION 822 catalyst).

The Blends were impregnated with V as follows:

Calcine the sample for 1 hour at 216°C (400°F); then, raise the temperature to 674°C (1250°F) and hold for 3 hours. Allow the sample to cool to room temperature. Impregnate the sample with vanadium naphthenate to give the desired amount of vanadium on the sample.

Calcine the vanadium naphthenate impregnated sample for 1 hour at 216°C (400°F), then raise the temperature to 782°C (1450°F) and hold for 1 hour. Allow the sample to cool to room temperature.

In a fluidized bed, carry out the following cycle 30 times at 782°C (1450°F), 50% steam and 0 psig. One cycle consists of a 10 minute purge with N_2, 10 minute stream of 5% propylene in air, and 10 minute purge of N_2 followed by a 10 minute exposure to an air stream containing 4000 ppm SO_2 and 10 minute purge of N_2. During the whole cycle, a flow of 50% steam is used.

The properties of the V-containing FCC/Additive samples (Blends A, B, C) are summarized in Table II.

TABLE II

Composition (wt.%)	100% FCC	90% FCC 10% (25% La_2O_3 + 75% clay)	90% FCC 10% (50% La_2O_3 + 50% clay)
Additive Sample No.	None	3	5
Blend No.	A	B	C
V ppm	5590	5610	5450
RE_2O_3 (wt.%)	1.51	3.70	5.68
Peak Ht. (X-ray)	31	34	33
Unit Cell (A)	24.22	24.21	24.22
Zeolite SA (m^2/g)	85	101	105
Matrix SA (m^2/g)	28	32	32

Example 4

Evaluation of FCC/Additive Mixtures

The FCC/Additive mixtures of Example 3 were evaluated for the catalytic cracking of a gas-oil feedstock. MAT evaluation was conducted using the procedure set forth in ASTM 3907. The kinetic conversion, coke selectivity, hydrogen selectivity and hydrogen/methane selectivity were determined at various catalyst/oil (cat/oil) ratios expressed as wt.% and conversion levels. The resulting data for Blends A, B,

and C is summarized in Figures 1, 2, 3 and 4. The letter labels on the curves correspond to the respective blends.

Example 5

A lanthanum oxide slurry was prepared by vigorously mixing 1579 g of La_2O_3 in 13.4 kg of water. 942 g of formic acid solution (45 wt.% formic acid) was added to the slurry followed by vigorous mixing for 15 minutes. 1059 g of kaolin clay and 843 g of alumina (VERSAL 900 from LaRoche Chemical Co.) and 800 g of water were added to the slurry. The resulting slurry was then mixed in a high shear mixer, then milled in a DRAIS mill, and spray dried. The spray dried material was then calcined for 1 hour at 593 °C in a muffle furnace. The resulting product had an average particle size of 58 μm, average bulk density of 0.85, 32 m^2/g surface area, and a DI of 8.

Example 6

15.8 lbs. rare earth oxide (calcined Molycorp 5211 rare earth carbonate) were added to an agitated heel of 99.6 lbs. water on a mix tank. 2.7 lbs formic acid solution (45 wt.% formic acid) were added to the slurry over about 6 minutes. 48.6 lbs. alumina (VERSAL 700 from LaRoche Chemical Co.) were added to the slurry over 90 minutes with vigorous agitation. 83.3 lbs. of dilution water were then added to the slurry over 10 minutes. The resulting mixture was then DRAIS milled and spray dried. The spray dried material was then calcined at 677 °C in a rotary calciner. The resulting product had an average particle size of 77 μm, average bulk density of 0.87, and a DI of 1.

Example 7

An aqueous rare earth chloride solution containing approximately 60 wt.% La on an oxide basis was combined with kaolin clay and water to form a slurry having a

solids content of about 10 wt.%. The slurry was milled, spray dried, and calcined at 649 °C for 1 hour in a muffle furnace to yield a composition containing 25 wt.% RE_2O_3 and 75 wt.% kaolin. The composition had an attrition index of about 8, an average bulk density of 0.92 and an average particle size of 46 μm.

Example 8

An aqueous rare earth chloride solution containing approximately 60 wt.% La on an oxide basis was combined with kaolin clay, water and colloidal silica (LUDOX brand) to form a slurry having a solids content of about 10 wt.%. The slurry was milled, spray dried, and calcined at 649 °C for 1 hour in a muffle furnace. The resulting particles were then washed with an ammonium hydroxide solution (pH=8) at about 70 °C to yield a composition containing 40 wt.% RE_2O_3 and 35 wt.% kaolin and 25 wt.% SiO_2 (from the colloidal silica). The composition had an attrition index of about 4, an average bulk density of 1.04 and an average particle size of 77 μm.

Example 9

An aqueous rare earth chloride solution containing approximately 60 wt.% La on an oxide basis was combined with kaolin clay, silica ID xerogel, and water to form a slurry having a solids content of about 10 wt.%. The slurry was milled (Prater mill), spray dried and calcined at 649 °C for 1 hour in a muffle furnace to yield a composition containing 40 wt.% RE_2O_3, 35 wt.% kaolin, and 25 wt.% xerogel. The composition had an attrition index of about 11, an average bulk density of 0.85 and an average particle size of 64 μm.

Example 10

In order to demonstrate the utility of the materials (traps) of examples 7-9 for trapping vanadium in FCC operation, the following study was carried out: a 100 g (on a dry basis) blend was prepared by mixing one of the traps prepared above with an

ORION 822 (GRACE-Davison) FCC catalyst at a weight ratio of 1 part trap to 9 parts FCC catalyst. An unblended, 100 g of FCC catalyst was taken as a base case. Each sample spread over a dish in a shallow bed was then treated according to the following protocol: Heated in a muffle furnace to 204°C air, allowed to soak for one hour at this temperature; raised to 503° C, allowed to soak for 3 hours at this temperature; and then allowed to cool to room temperature; impregnated with a desired level - 5000 ppm in this study - of vanadium naphthenate in pentane to completely and uniformly cover all particles with vanadium; allowed pentane to evaporate away in muffle furnace at room temperature; heated to 204°C and held for one hour; raised to 593°C, and allowed to soak at this temperature for 3 hours; and then allowed to cool to room temperature; charged into an Inconel fluid-bed reactor; allowed the bed temperature to reach 771°C in flowing nitrogen over a period of approximately 3 hours; and then subjected to 20-hour/771°C cyclic-propylene-steaming (CPS), an accelerated catalyst deactivation protocol involving redox cycles (40 minutes/cycle) and 50 weight % steam (10 g H_2O/hour) throughout each cycle as follows: 10 minutes of nitrogen (137 ml/min.), 10 minutes of nitrogen containing 5 vol.% propylene, 10 minutes of nitrogen, and 10 minutes of air containing 4000 ppm SO_2 finally, the reactor was allowed to cool to room temperature in flowing nitrogen for discharging the sample.

In the course of the above deactivation treatment, FCC catalysts are attacked by vanadium. In the presence of a metals trap, however, the degree of vanadium attack on FCC catalysts can be significantly lessened as a result of vanadium capture by the metals trap. In order to prove this, each of the above deactivated samples was divided into two fractions - approximately 10 weight % of sink (metals trap) and approximately 90 weight % of float (FCC catalyst) fractions - by means of so-called "sink-float" or density separation, using tetrabromoethane having a density of 2.96 g/ml, tetrachloroethane having a density of 1.58 g/ml, and a centrifuge. All the samples, before and after the sink-float separation, were analyzed by using an Inductively Coupled Plasma Spectrometer. The so-called vanadium pick-up factor (V-PUF) was determined for each of the compositions of examples 7-9. The V-PUF,

defined by the ratio of vanadium concentration in the trap (i.e., in the sink fraction) to that in the FCC catalyst (i.e., in the float fraction), is a measure of vanadium trapping efficiency. The V-PUF for examples 7-9 were 4.4, 4.7, and 9.6 respectively.

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Claims

What is claimed is:

1. A composition comprising inorganic oxide particles bound by a rare earth compound binder.

2. The composition of Claim 1 further comprising an auxiliary binder.

3. The composition of Claim 1 wherein said rare earth compound binder comprises rare earth compounds selected from the group consisting of oxides, oxychlorides, oxycarbonates, and mixtures thereof.

4. The composition of Claim 1 wherein said rare earth compounds comprise rare earth metals selected from the group consisting of lanthanum, neodymium, cerium and mixtures thereof.

5. The composition of Claim 1 wherein said inorganic oxide particles comprise materials selected from the group consisting of zeolites, clays, silica, alumina, silica alumina, rare earth oxides, and mixtures thereof.

6. The composition of Claim 2 wherein said auxiliary binder is selected from the group consisting of peptized alumina and colloidal silica.

7. The composition of Claim 1 wherein said rare earth compound binder is derived from an acid-peptized rare earth sol.

8. The composition of Claim 4 wherein said rare earth metal consists essentially of lanthanum.

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9. The composition of Claim 4 wherein the rare earth compound comprises at least about 50 weight percent lanthanum expressed as La_2O_3.

10. The composition of Claim 1 wherein at least a portion of said inorganic oxide particles are silica gel particles.

11. The composition of Claim 1 wherein said inorganic oxide particles comprise zeolites selected from the group consisting of zeolites X, Y, REY, USY, Beta, ZSM-5, and mixtures thereof.

12. The composition of Claim 1 wherein said inorganic oxide particles comprise materials selected from the group consisting of clays, silica, alumina, silica alumina, rare earth oxides, and mixtures thereof.

13. The composition of Claim 12 wherein said inorganic oxide particles consist essentially of alumina.

14. The composition of Claim 12 wherein said inorganic oxide particles consist essentially of clay.

15. The composition of Claim 1 wherein the composition itself is in the form of particles having a particle size of 10 to 150 mm.

16. A catalytic cracking catalyst composition comprising a zeolite-containing fluid cracking catalyst admixed with additive particles comprising inorganic particles selected from the group consisting of clays, silica, alumina, silica alumina, rare earth oxides, and mixtures thereof, said inorganic particles being bound by a rare earth compound binder.

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17. The composition of Claim 16 wherein said additive particles have a particle size of about 10 to 150 mm.

18. A method for the catalytic cracking of hydrocarbons which comprises reacting a vanadium-containing hydrocarbon feedstock in the presence of the catalyst of Claim 16 under catalytic cracking conditions.

19. A method for preparing a particulate composition comprising inorganic particles bound by a rare earth compound binder, said method comprising:

(a) mixing a rare earth compound sol or rare earth salt solution with said particles to be bound to form a mixture,

(b) forming the resulting mixture into particles, and

(c) calcining the mixture particles to obtain particles which themselves comprise the particles added in step (a) bound by a rare earth compound phase.

20. The method of Claim 19 wherein said particle forming in step (b) comprises spray drying said mixture.

21. The method of Claim 19 wherein said calcining is conducted at a temperature of 400 to 800°C.

22. The method of Claim 19 wherein said rare earth compounds are selected from the group consisting of oxides, oxychlorides, oxycarbonates, and mixtures thereof.

23. The method of claim 19 wherein a rare earth sol is used in step (a), said rare earth sol being formed by peptizing a rare earth compound particles with a monobasic acid.

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24. The method of claim 23 wherein the amount of monobasic acid used is in excess of that needed to form said rare earth sol and wherein alumina particles are added to said rare earth sol containing said excess monobasic acid to thereby for an auxiliary binder of peptized alumina.

25. The method of claim 19 wherein an auxiliary binder is added to the mixture of step (a) before step (b).

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