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54 **Catalytic cracking catalyst and process.**

57 Catalytic cracking catalysts which contain a basic alkaline earth metal component in amounts greater than 5 percent by weight (expressed as the oxides) are used to crack hydrocarbon feedstocks that contain substantial quantities of metals such as vanadium, nickel, copper and iron. In a particularly preferred embodiment natural or synthetic particulate magnesium oxide (MgO) containing composites such as a formed particulate coprecipitated magnesia-silica cogel (MgO.SiO₂) having a substantial intraparticle pore volume in pores ranging from about 20-10,000 Å in diameter and an average pore diameter greater than about 400 Å in the 20-10,000 Å diameter range is mixed with a zeolite containing fluid cracking catalyst (FCC) either as an integral component of the catalyst particle or as a separate additive.

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CATALYTIC CRACKING CATALYST AND PROCESS

The present invention relates to catalytic cracking catalysts, and more specifically to cracking catalyst compositions which are particularly effective for the cracking of residual type hydrocarbon feedstocks.

In recent years, the refining industry has been required to process ever increasing quantities of residual type feedstocks. These heavy feedstocks are frequently contaminated with substantial quantities of metals such as vanadium, nickel, iron and copper which adversely affect cracking catalyst used in refinery operations.

Zeolite containing cracking catalysts in particular are susceptible to deactivation (poisoning by vanadium) and in addition the catalytic selectivity of the catalyst is adversely affected by the presence of iron, copper and nickel.

U.S. 3,835,031 and U.S. 4,240,899 describe cracking catalysts which are impregnated with Group IIA metals for the purpose of reducing sulfur oxide emissions during regeneration of the catalyst.

U.S. 3,409,541 describes catalytic cracking processes wherein deactivation of the catalyst by contaminating metals is decreased by adding to the catalytic inventory a finely divided alkaline earth or boron type compound which reacts with the metal contaminants to form an inert product that may be removed from the catalytic reaction system.

U.S. 3,699,037 discloses a catalytic cracking process wherein a finely divided additive such as calcium and magnesium hydroxides, carbonates, oxides, dolomite and/or limestone is added to the catalyst inventory to sorb SO_x components present in the regenerator flue gas.

U.S. 4,198,320 describes catalytic cracking catalysts which contain colloidal silica and/or alumina additives that are added for the purpose of preventing the deactivation of the catalyst when used to process metals containing feedstocks.

U.S. 4,222,896 describes a metals tolerant zeolite cracking catalyst which contain a magnesia-alumina-aluminum phosphate matrix.

U.S. 4,283,309 and 4,292,169 describe hydrocarbon conversion catalysts which contain a metals-absorbing matrix that includes a porous inorganic oxide such as alumina, titania, silica, zirconia, magnesia and mixtures thereof.

U.S. 4,465,779 discloses cracking catalyst compositions which comprise a high activity catalytic cracking catalyst and as a separate and distinct entity a magnesium compound or magnesium compound in combination with a heat stable compound.

U.S. 4,432,890 and 4,469,588 disclose catalytic cracking catalyst compositions which are used to crack hydrocarbon oil feedstocks that contain significant quantities of vanadium which comprise a zeolite and an amorphous inert solid matrix containing a metal additive such as magnesium which may be introduced into the catalyst during manufacture or during use in the conversion of hydrocarbons.

PCT WO 82/00105 discloses cracking catalysts that are resistant to metals poisoning which comprise two particulate size fractions, and an SO_x absorbing additive such as aluminum oxide, calcium oxide and/or magnesium oxide.

While the prior art suggests several catalytic systems and compositions which are effective in controlling the adverse poisoning effects of metals contained in residual type feedstocks or limiting SO_x emissions during regeneration of the catalyst, many of the systems require the use of expensive additives and/or processing systems and are not particularly cost effective when operated on a commercial scale.

It is therefore an object of the present invention to provide improved catalytic cracking catalysts which are capable of cracking hydrocarbon feedstocks that contain substantial quantities of metals and sulfur

It is another object to provide fluid cracking catalysts (FCC) which are resistant to metals poisoning and which may be recharged and used in large quantities at reasonable cost.

It is a further object to provide a catalytic cracking process which is capable of handling large quantities of metals, vanadium in particular, without substantial loss of activity or product yield.

These and still further objects of the present invention will become readily apparent to one skilled in the art from the following detailed description and specific examples.

Broadly, the invention contemplates catalytic cracking catalysts which include a basic alkaline earth metal component in amounts ranging from about 5 to 80 weight percent expressed as the oxides, wherein the catalyst is capable of maintaining a high degree of activity when associated with substantial quantities of deactivating metals such as vanadium deposited on the catalyst.

More specifically, it has been found that particulate basic alkaline earth metal compositions are useful which have an intra-particle pore structure characterized by a pore volume of at least 0.1 cc/g in pores having a diameter of about 200 to 10,000

A°, and an average pore diameter (APD) of greater than about 400 A° when determined in the pore size range of about 200 to 10,000 A° diameter using the relationship:

$$\text{APD} = \frac{4 \times 10^4 \times \text{PV}}{\text{SA}}$$

wherein PV = pore volume in cc/g in pores ranging from 200-10,000 A° diameter and SA = surface area in m²/g in pores ranging from 200-10,000 A° diameter, as determined by mercury porosimetry.

The alkaline earth metal compound used in the practice of the invention is selected from group IIA of the periodic Table with calcium and magnesium being preferred and magnesium the most preferred. In a particularly preferred embodiment of the invention the basic alkaline earth metal component comprises

MgO or magnesia-silica gels

and a significant pore volume in pores greater than about 400 A° at process temperatures of 1400°F or so.

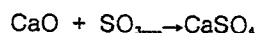
In a particularly preferred embodiment a magnesium oxide containing component such as a magnesia-silica gel (MgO.SiO₂) is prepared in a particulate form wherein the particle has a substantial pore volume in pores having a diameter of greater than about 400°A. The resulting MgO.SiO₂ composition is included in a FCC catalyst composition either as an integral component of the FCC catalyst particle or more preferably as a separate particulate additive in amounts ranging from about 2.5 to 40 by weight of the composition.

The preferred MgO.SiO₂ gel has the overall weight composition of 30-80% MgO, and a pore volume in pores greater than about 400°A diameter of at least 0.1 cc/g and preferably from about 0.2 to 1.0 cc/g. Where the MgO.SiO₂ gel is added to a FCC catalyst as a separate particulate additive, the particle size and density of the additive is preferably similar to that of the FCC catalyst, i.e. particle size range of about 40 to 80 microns and an average bulk density of 0.5 to 1.0 g/cc.

A preferred MgO.SiO₂ gel is prepared by reacting aqueous sodium silicate and magnesium chloride solutions at a temperature of about 15 to 50°C to form a precipitate gel which is recovered by filtration, reslurried in water and spray dried at a

temperature of about 330 to 500°C. Furthermore, particulate MgO can be added to the MgO.SiO₂ gel to give composition of 30-80% MgO to the final product.

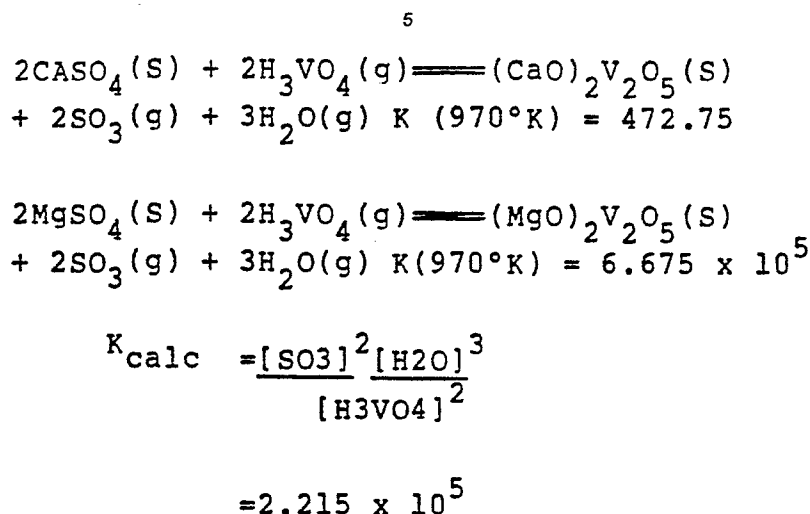
As indicated above, the MgO containing catalyst component must have the optimized pore structure described above in order to be effective for vanadium scavenging. This is due to the fact that partial molar volume of magnesium vanadate is greater than magnesium oxide. It is believed that the vanadium poisoning of cracking catalysts is caused by the poison precursor H₃VO₄ which is formed in the regeneration step from the reaction of V₂O₅ and steam (for vapor pressure data see L.N. Yannopoulos, *J. Phys. Chem.* **72**, 3293 (1968). H₃VO₄ is isoelectronic with H₃PO₄ and is most probably a strong acid. H₃VO₄ therefore destroys the zeolite crystallinity and activity by acid hydrolysis of the SiO₂-Al₂O₃ framework of the zeolite. As H₃VO₄ reacts with MgO and forms (MgO)₂V₂O₅ on the surface of pore, the surface of the pore will swell due to larger molar volume of (MgO)₂V₂O₅. If the pore is too small, blocking will occur readily and thereby inhibit the further reaction with H₃VO₄. We have experimentally determined that the average pore diameter must be greater than 400°A or so to be effective. This effect has been extensively studied with similar reaction:



(see S.K. Bhatia and D. D. Perlmutter *AIChE J.* **27**, 266 and **29**, 79).

As indicated above, MgO is the preferred oxide over the other alkaline earths when used in conjunction with FCC catalysts. This is due to the presence of sulfur oxides in the flue gases of the regenerator, which can compete with H₃VO₄ forming alkaline earth SO₄'s as shown by a consideration of the equilibrium constants for the reactions of MgSO₄ and CaSO₄ with vanadic acid. Assuming a worst case test in which all of the SO_x is assumed to be SO₃ at a typical level of 2000 ppm in the regenerator, 20% H₂, 1.07 ppm H₃VO₄ and a temperature of 970°K (1285°F) a calculated equilibrium constant (assuming unit activity for the con-

densed phases) from the regenerator conditions above can be compared to the equilibrium constant for the two reactions from thermochemical data as follows:



For the case of calcium the calculated equilibrium from regenerator conditions is much greater than the equilibrium constant for the reaction. By the Le Chatelier's principle the reaction will favor the left hand side of reaction with calcium. The opposite is true for the case with MgO. If calcium is used CaSO₄ will be preferentially formed over the vanadate, the opposite is true for magnesium.

The fluid catalytic cracking catalysts which are combined with the basic alkaline earth metal component, are conventional and well known to those skilled in the art. Typically, the catalysts comprise amorphous inorganic oxide gels such as silica-alumina hydrogels, and/or a crystalline zeolite dispersed in an inorganic oxide matrix.

Preferred zeolites are synthetic faujasite (type Y zeolite) and/or shape selective zeolites such as ZSM-5. Type Y zeolites which are exchanged with hydrogen and/or rare earth metals such as HY and REY, and those which have been subjected to thermal treatments such as calcined, rare-earth exchanged Y (CREY) and/or Z14US are particularly suited for inclusion in fluid cracking catalyst compositions. Catalytically active zeolite components are typically described in U.S. patents 3,293,192 and RE 28,629.

In addition to an active zeolite component, the catalysts contain an inorganic oxide matrix. The inorganic oxide matrix is typically a silica-alumina hydrogel, which may be combined with substantial quantities of clay such as kaolin. In addition, it is contemplated in catalyst matrix systems which comprise silica, alumina, silica-alumina sols and gels may be utilized in the practice of the present

invention. Methods for producing suitable catalyst compositions are described in U.S. 3,974,099, 3,957,689, 4,226,743, 3,867,308, 4,247,420, and U.S. Serial No. 361,426 filed March 24, 1982.

The basic alkaline earth metal component may be added to the catalyst composition in the form of a finely divided particulate solid or the component may be added in the form of a salt which is subsequently converted to a solid oxide. Magnesium and calcium oxides, hydroxides, carbonates or sulfates are particularly suited forms of the basic alkaline earth metal components which are added to the catalyst either during or after manufacture. In one preferred embodiment, the basic alkaline earth containing component is physically admixed with the particulate catalyst. In another preferred embodiment, the alkaline earth metal component is included in the catalyst composition (matrix) during manufacture. In order to obtain the maximum degree of metals tolerance while avoiding undue deactivation of a zeolite component which may be present in the catalyst, the alkaline earth metal component is added to the zeolite containing catalyst in a form that does not ion exchange with the zeolite component.

In a typical FCC catalyst preparation procedure in which the component is added to the catalyst composition, a finely divided alkaline earth metal component is blended with an aqueous slurry which contains silica-alumina hydrogel, optimally a zeolite, and clay to obtain a pumpable slurry which is then spray dried to obtain microspheroidal particles of catalyst having a particle size ranging from about 20 to 100 microns. The spray dried catalyst, which typically contains from about 0 to 35 percent

by weight zeolite, 25 to 70 percent by weight clay, and 10 to 50 percent by weight matrix binder, such as silica, alumina, silica-alumina hydrogel or sol, and from 5 to 80 percent by weight alkaline earth metal component, is washed and ion exchanged to remove soluble impurities such as sodium and sulfates. After drying to about 10-30 percent total volatiles the catalyst is ready to be used in conventional catalytic cracking processes. Typical FCC processes involve contact of the catalyst with a hydrocarbon feedstock which may contain significant quantities, i.e. from 1 to 200 ppm of vanadium and other metals such as nickel, iron and copper at temperatures on the order of 900 to 1000°F to obtain cracked products of lower molecular weight such as gasoline and light cycle oil.

It is found that during the catalytic cracking process, the catalysts contemplated in the present invention can sorb in excess of 0.1 percent and up to 10 percent by weight of metals, particularly vanadium, while maintaining an acceptable level of activity and product selectivity. Typical "conventional" catalysts, which do not contain the alkaline earth metal component contemplated herein, lose substantial activity when the metals content (vanadium in particular) exceeds about 0.1 weight percent.

Having described the basic aspects of the present invention, the following examples are given to illustrate the specific embodiments thereof.

Example 1

This example shows the preparation and use of large and small pore MgO based vanadium scavenging additives. A magnesia-silica gel was prepared by mixing a 3.62% SiO₂ and 10.87% NaOH aqueous solution with 13.28% MgCl₂ aqueous solution at equal flow rates through a mix

pump to form a MgO.SiO₂ gel with composition 60 wt.% MgO 40 wt.% SiO₂. The temperature of the reaction mixture was 30°C for example A to make smaller pore diameters, and 20°C for example B for larger pore diameters. The resultant gel in both cases was filtered, reslurried in water to ~10% solids and spray dried at 330°C. The spray dried material was washed with 70°C H₂O to remove NaCl. Both preps were calcined for 2 hours at 538°C.

Two catalyst samples were prepared by blending 20 % by weight of additive A or B with 80 % by weight of a commercial FCC catalyst (Super D). The so obtained catalyst samples were impregnated to a level of 0.67 wt % vanadium, using a solution which contained vanadyl oxylate dissolved in water. The samples were then pre-heated at 900°F for 1 hour and then 2 hours at 1400°F. The catalyst samples were then subjected to a hydrothermal deactivation treatment which involved contacting the catalyst with 100 % steam at a pressure of 2 atm at 1350°F for 8 hours. The catalysts of this Example (as well as the catalysts evaluated in Example 2) were then tested for catalytic cracking activity using the microactivity test described in ASTM D-3907. The microactivity - (MA) of the catalyst samples is expressed in terms of volume percent (vol%) of feedstock converted. The results are summarized in Table I set forth below.

Analytical data in Table V shows the two Samples have similar properties except that the metals tolerance of an 80% commercial FCC catalyst - (Super D) 20% additive (either A or B) was dramatically improved for example B. This example clearly demonstrates the importance of the larger pore volume and APD for vanadium scavenging effectiveness.

TABLE I
Analytical and Metals Data for Two MgO Additives

	<u>Theoretical Composition</u>	
	60% MgO 40% SiO ₂	
	(12817-75A) <u>A</u>	(12817-58A) <u>B</u>
Run-off Temp.	30°C	20°C
MgO	64.07	62.58
SiO ₂	38.40	36.41
PV (20°-10,000) cc ² /g	.065	.194
APD (20°-10,000) A°	703	624
Metals impregnation of 80% Super D, 20% Additive with .67% V. S-13.5 steam.		
MA	17	41
H ₂ (vol%)	.30	.16
Coke (wt%)	2.10	1.65

Example 2

This example again shows the use of high pore volume and low pore volume MgO. Catalyst A is a blend of 80 % Super D, 20% commercially available high pore volume MgO (from Martin Marietta

grade Mag-Chem-30). Catalyst B is a blend of 80% Super D, 20% commercially available low pore volume MgO (from Martin Marietta grade Mag-Chem 10). Both catalysts are impregnated by the procedure in Example 1. Table VI shows the microactivity results.

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TABLE II

	<u>Catalyst A</u>	<u>Catalyst B</u>
PV (20°-10,000) m ² /g	.821	.065
APD (20°-10,000) A°	1,266	3,466
0% VMA	67	67
H ₂ /C	.06/2.30	.04/1.73
.67% VMA	55	13
H ₂ /C	.08/1.82	.06/.75
1.34% VMA	38	11
H ₂ /C	.11/1.51	.091

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Claims

1. A catalytic cracking catalyst composition which comprises:

(a) a cracking catalyst component, and

(b) from about 5 to 80 percent by weight expressed as the oxides of a basic alkaline earth metal component wherein said component is characterized by a pore volume of at least 0.1 cc/g and an average pore diameter greater than about 400 Å in pores having diameter of 200-10,000 Å.

2. The composition of claim 1 which contains greater than 0.1 percent by weight vanadium deposited on the catalyst during use in a catalytic cracking process.

3. The composition of claim 2 which contains from about 0.1 to about 10 percent by weight vanadium.

4. The composition of claim 1 wherein the catalyst component comprises synthetic faujasite dispersed in an inorganic oxide matrix.

5. The composition of claim 4 wherein said inorganic oxide matrix comprises silica-alumina gel and clay.

6. The composition of claim 1 wherein said basic alkaline earth metal compound is selected from the group consisting of calcium and/or magnesium oxides, carbonates, acid salts and mixtures thereof.

7. The composition of claim 1 wherein said basic alkaline earth metal component comprises a magnesia-silica gel having the weight composition 30 to 80 % MgO.

8. The composition of claim 1 wherein said basic alkaline earth metal compound is dispersed in said matrix as a separate oxide phase.

9. The composition of claim 1 wherein said basic alkaline earth metal component is physically mixed as a separate particulate additive.

10. In a method for the catalytic cracking of metals containing hydrocarbons wherein said hydrocarbon is reacted under catalytic cracking conditions with a catalyst, and deactivating metals including vanadium are deposited on said catalyst, the improvement comprising:

Conducting the reaction using the catalyst of claim 1.

11. A composition for scavenging vanadium which comprises a magnesia-silica gel having the weight composition 30 to 80% MgO and a pore volume of at least 0.1 cc/g and an average pore diameter greater than about 400 Å diameter in pores ranging from about 200 to 10,000 Å in diameter.

12. The composition of claim 11 wherein said composition has a total pore volume of 0.2 to 1.0 cc/g.

13. The composition of claim 11 wherein the composition is formed into particles having a size range of 40 to 80 microns.

14. The composition of claim 13 wherein the particles have a density of about 0.5 to 1.0 g/cc.

15. The method of claim 10 wherein said catalyst comprises a crystalline zeolite dispersed in an inorganic oxide matrix.

16. The method of claim 15 wherein said zeolite is synthetic faujasite.

17. The method of claim 16 wherein said zeolite is calcined rare earth exchanged type Y zeolite.

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 86106616.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	US - A - 4 439 312 (ASAOKA et al.) * Claims; column 3, line 60 - column 13, line 48 * --	1,2	C 10 G 11/02 B 01 J 29/06
A	US - A - 4 399 026 (SHIROTO et al.) * Claims; column 4, line 17 - column 14, line 60 * --	1,2	
A	GB - A - 2 063 700 (CHIYODA CHEMICAL ENGINEERING & CONSTRUCTION CO. LTD.) * Claims; page 2, lines 6-56 * --	1,2	
A	DE - B2 - 2 163 756 (W.R. GRACE & CO.) * Claims; examples 1,2 * ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 10 G 11/00 C 10 G 47/00 B 01 J
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 22-09-1986	Examiner STÖCKLMAYER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			