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[11] E

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[54] **BARIUM TITANIUM OXIDE-CONTAINING
FLUIDIZABLE CRACKING CATALYST
COMPOSITION**

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Related U.S. Patent Documents

Reissue of:

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502/84; 502/516; 502/521

[58] **Field of Search** **502/64, 65, 68,**
502/84, 516, 521

[56] **References Cited****U.S. PATENT DOCUMENTS**

2,730,487 1/1956 Porter et al. 196/24
2,862,875 12/1958 Morrell 208/119
2,886,513 5/1959 Baker 208/121
3,252,757 5/1966 Granquist 23/111
3,252,889 5/1966 Capell et al. 208/120
3,471,410 10/1969 Oleck et al. 502/64
3,472,791 10/1969 Vesely et al. 252/448
3,609,103 9/1971 Gladrow et al. 252/455 Z
3,676,330 7/1972 Plank et al. 252/455 Z
3,743,594 7/1973 Mulaskey 208/216
3,985,639 10/1976 Suggitt et al. 208/120
3,985,641 10/1976 Finch et al. 208/121
4,107,088 8/1978 Elliott, Jr. 252/455 Z
4,126,579 11/1978 Flaherty, Jr. et al. 252/455 Z

4,179,409 12/1979 Gladrow et al. 208/120
4,182,693 1/1980 Gladrow 252/455 Z
4,243,514 1/1981 Bartholic 208/91
4,263,128 4/1981 Bartholic 208/91
4,432,890 2/1984 Beck et al. 502/62
4,451,355 5/1984 Mitchell et al. 208/113
4,473,463 9/1984 Bertus et al. 208/120
4,496,665 1/1985 Hettinger, Jr. 502/521
4,520,120 5/1985 Mitchell et al. 502/68
4,522,937 6/1985 Yoo et al. 502/303
4,770,765 9/1988 Bartek et al. 208/113
4,944,864 7/1990 Kugler 208/120

FOREIGN PATENT DOCUMENTS

0063712 3/1982 European Pat. Off. .
0194536 9/1986 European Pat. Off. .
020924 1/1987 European Pat. Off. .
3518094 11/1985 Germany 502/64
2138314 10/1984 United Kingdom .
8203226 9/1982 WIPO .

OTHER PUBLICATIONS

Wells, A. F.; *Structural Inorganic Chemistry*, 1962, Third Edition.

"Phase Equilibria in the System BaO-TiO₂" by D. E. Rase & Rustum Roy *Journal of the American Ceramic Society*, vol. 38, No. 3, pp. 102-113.

"The Ternary Systems BaO-TiO₂-SnO₂ and BaO-TiO₂-ZrO₂", by G. H. Jonker & W. Kwestroo, *Journal of The Amer. Ceramic Soc.*, vol. 41, No. 10, pp. 390-394.

"Phase Equilibria in the TiO₂-Rich Region of the System BaO-TiO₂", by H. M. O'Bryan, Jr., & J. Thompson, Jr., *Journal of the American Ceramic Society*, vol. 52, No. 12, pp. 522-526.

Akzo Chemie, *Ketien Catalyst* 1982, pp. 80-84.

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[57] **ABSTRACT**

A cracking catalyst composition comprising a zeolitic, crystalline aluminosilicate, a matrix material and a barium titanium oxide. The catalyst composition is particularly suitable for cracking metal-containing hydrocarbon feedstocks.

19 Claims, No Drawings

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BARIUM TITANIUM OXIDE-CONTAINING FLUIDIZABLE CRACKING CATALYST COMPOSITION

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

BACKGROUND OF THE INVENTION

The present invention relates to a fluidizable cracking catalyst composition comprising a zeolitic, crystalline aluminosilicate, a matrix material and a barium compound. A catalyst composition of this type is suitable for cracking oil feedstocks and is disclosed in U.S. Pat. No. 4,473,463. According to the description in that patent, barium compounds are incorporated into or applied onto cracking catalysts to prevent deleterious effects caused by metal contamination in oil feedstocks. The catalysts generally contain a silica-alumina matrix in which zeolitic materials are embedded. Preferably, use is made of barium acetyl acetonate. In this U.S. patent, the results obtained are described in an example in which a cracking catalyst contaminated with metals is re-activated in a treatment with barium acetyl acetonate. This compound, however, and many other barium compounds are not quite suitable to be used for composing a metal resistant cracking catalyst, as appears from metal resistance and micro-activity tests (referred to as MR test and MAT test, respectively).

A barium compound in which the cracking catalyst composition is of the above well-known type but which contains a barium titanium oxide has now been found which does not show the above drawback.

Use of barium compounds in cracking catalysts is also known from other patent specifications. U.S. Pat. No. 4,179,409 describes a cracking catalyst which in addition to a zeolite and an inorganic oxide gel matrix contains a perovskite. As a result, the cracked oil will have a higher octane number. The perovskite may be a barium compound, such as barium zirconate (BaZrO_3).

In the cracking process of EP No. 0 063 712, use is made of metal traps, such as type A zeolite, which may contain for instance a barium compound. It should be added that U.S. Pat. No. 4,451,355 relates to a cracking catalyst which in addition to a zeolitic aluminosilicate and a matrix material contains a calcium-containing additive for trapping metal contaminations. Particular calcium/titanium-containing compounds, including calcium titanate (CaTiO_3), are considered to be particularly suitable for this purpose.

SUMMARY OF THE INVENTION

The present invention provides a cracking catalyst composition comprising a zeolitic, crystalline aluminosilicate, a matrix material and a barium titanium oxide. The catalyst composition is particularly suitable for cracking metal-containing hydrocarbon feedstocks.

DETAILED DESCRIPTION OF THE INVENTION

The barium titanium oxides that may be included in the present catalyst composition are described by, inter alia, D. E. Rase and R. Roy in J. Amer. Ceram. Soc. 38, 108 (1955), G. H. Jonker and W. Kwestroo in J. Amer. Ceram. Soc. 41, 390 (1958) and H. M. O'Bryan and I. Thomson in J. Amer.

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Ceram. Soc. 57, 522 (1974). Examples of suitable barium titanium oxides include Ba_2TiO_4 , BaTiO_3 , $\text{Ba}_2\text{Ti}_5\text{O}_{12}$, $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$, BaTi_3O_7 , $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$, BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. Particularly suitable are Ba_2TiO_4 , BaTi_3O_7 , and especially BaTiO_3 (barium titanate).

As the zeolite crystalline aluminosilicate may be used all molecular sieves commonly employed for cracking catalysts. It is preferred that use should be made of synthetic crystalline aluminosilicates having a pore diameter in the range of 3 to 15 angstroms. Examples thereof include the zeolites A, X, Y, ultrastabilized sieves, ZK-4, ZK-5, ZSM-5, ZSM-11 and ZSM-12. It is preferred that zeolites of the types X, Y and/or ultrastabilized sieves should be applied. To ensure proper catalyst activity the cations of these zeolites, which are often prepared in the sodium form, need to be exchanged. For this ion exchange, use is generally made of solutions containing rare earth metal ions and/or ammonium or hydrogen ions. The exchange is as a rule carried on to such a level that the zeolites and the ready catalyst contain less than 4% by weight, preferably less than 0.5% by weight, of sodium.

As matrix material can be used all well-known matrix materials suitable for embedding zeolitic, crystalline aluminosilicates, such as silica, alumina, magnesia, zirconia, titania, boris, aluminum chlorohydrate and mixtures thereof. Preference is given to silica, silica-alumina and alumina.

In addition to the barium titanium oxide and the aluminosilicate, other components may also be incorporated into the matrix material. As examples thereof may be mentioned clays such as kaolin, bentonite and layered clays as discussed in U.S. Pat. Nos. 3,252,757, 3,252,889 and 3,743,594, montmorillonite, etc.

To augment the octane number of the petrol fraction produced, alumina particles as described in U.S. Pat. No. 4,182,693 may be incorporated into the catalyst composition.

Moreover, use may be made of usual amounts of one or more passivators which may contain antimony, tin and the like. They particularly serve to prevent excessive formation of hydrogen during the cracking process.

To reduce SO_x emission and to promote the conversion of CO to CO_2 , an oxidation promoting metal or metal compound may be incorporated into the present composition. The cracking catalyst composition generally contains 0.05–1000 ppm of an oxidation promoting metal or metal compound. Suitable for that purpose are noble metals or compounds thereof of group VIII of the periodic system, such as Pt, Pd, Ir, Rh, Os and Ru. Also suitable to that end are rare earth metals or compounds thereof. Examples of suitable oxidation promoters also include Cr and Cu, and compounds thereof. It is preferred that use should be made of 0.1 to 100 ppm, more particularly 0.1–50 ppm of a noble metal of group VIII. Most preference is given to the incorporation into the catalyst of 0.1–10 ppm of platinum or palladium. These metals may be incorporated in the catalyst in a known manner, for instance by impregnation with a corresponding salt solution.

The components of the catalyst composition may be combined with the matrix material in a manner known in itself. Suitable methods of preparation are described, among other places, in U.S. Pat. Nos. 3,609,103 and 3,676,330. For instance, the barium titanium oxide and the aluminosilicate may be combined with the matrix material when the latter material is already in the gelled state. After proper mixing and subsequent spray drying the ready catalyst composition is obtained. Alternatively, the various components may be

added to a matrix material in the form of a sol. This sol bonding agent can be formed into a gel before or during spray drying. The latter procedure is to be preferred in that it permits obtaining catalyst compositions having a relatively high density. Thus, apparent densities higher than 0.5 g/ml, preferably higher than 0.70 g/ml are simple to realize.

A suitable catalyst composition according to the present invention comprises 5–50, preferably 10–30 percent by weight of a zeolitic, crystalline aluminosilicate and 0.01–30, preferably 1–20, more particularly 1–10 percent by weight of barium titanium oxide, which two components are embedded in 10–90 percent by weight of matrix material. It is preferred that the aluminosilicate should consist of a type Y zeolite or an ultrastabilized zeolite exchanged for rare earth metal ions and/or ammonium or hydrogen ions. The matrix material is preferably a silica, silica-alumina or alumina formed into a gel by spray drying the total composition. Particularly in uses requiring a reduction of SO_x emission, it is preferred that there should be incorporated 0.1–10 ppm of platinum into the catalyst composition.

The cracking catalyst composition may optionally consist of a physical mixture of:

a. catalytically active particles comprising a zeolitic crystalline aluminosilicate embedded in matrix material; and

b. catalytically less active particles comprising barium titanium oxide embedded in matrix material. This embodiment of the invention has the advantage that the amount of barium titanium oxide added can readily be adapted to the feedstock to be cracked.

Very suitable is a physical mixture in which:

a. the catalytically active particles contain 10–80, preferably 20–40 percent by weight of zeolitic, crystalline aluminosilicate, 5–60, preferably 20–50 percent by weight of clay and 5–85, preferably 10–30 percent by weight of silica, silica-alumina or alumina, and

b. the catalytically less active particles contain 10–80, preferably 10–40 percent by weight of barium titanium oxide, and 10–90, preferably 10–30 percent by weight of silica, silica-alumina, or alumina and, optionally, 10–50 percent by weight of clay.

Also in this mixture the silica, silica-alumina or alumina in the catalytically active and/or less active particles preferably consists of silica, silica-alumina or alumina formed into a gel by spray drying the respective particles. Especially if augmentation of the octane number of petrol fractions is envisaged, then aluminum oxide particles may be incorporated into the catalytically active and/or less active particles in an amount of up to in all 40, preferably 1–15 percent by weight of aluminum oxide particles.

It is also possible for the two different types of particles to have different diameters. For instance, the catalytically active particles may have a diameter of 80–125 microns and the catalytically less active particles a diameter of 30–75 microns.

Moreover, into one or more of the two components of the mixture a noble metal of group VIII of the periodic system may be incorporated in a concentration of 0.1–100 ppm,

preferably 0.1 to 50 ppm, calculated on the weight of the total mixture. It is again preferred then that platinum should be used in an amount of 0.1–10 ppm.

The present catalyst composition is suitable for use in a conventional process for cracking feeds. Catalytic cracking is normally carried out at a temperature of 375°–650° C., more particularly 460°–560° C. The pressure applied is generally in the range from atmospheric pressure to a pressure of 7 atmospheres, more particularly a pressure from 1 to 3 atmospheres. Regeneration with steam is generally carried out at 540°–825°, more particularly 750°–800° C. Suitable feeds include the hydrocarbon materials that are normally subjected to cracking.

The catalyst composition is particularly suitable for cracking metal-containing hydrocarbon feedstocks having a boiling range which generally ends at a temperature higher than 480° C., a density greater than 900 kg/cm³, metal concentration (Ni and V) of more than 1 ppm and a Conradson carbon content higher than 1%. The present catalyst composition, however, is preferably applied to heavier feeds, such as residues that include a substantial concentration of metals and/or asphaltenes.

If the feedstock has a high metal content, preference is given to a process in which the feedstock to be cracked is first brought into contact with the barium titanium oxide-containing particles and subsequently with the zeolite-containing particles. The feedstock will be demetallized then before cracking.

EXAMPLE 1

The catalyst compositions in Table 1 were obtained by mixing the various catalyst constituents with a silica-alumina sol. The total compositions were milled in a colloid mill, gelled by spray drying, and the resulting particles were exchanged with $(NH_4)_2SO_4$, and dried. The performance of the resulting catalyst compositions was measured by carrying out MAT and MR tests. The MAT test corresponds to test method D3907-80 of the American Society for Testing and Materials (ASTM). The MR test is described on pp. 80–84 of the Ketjen Symposium book, 1982, Amsterdam, The Netherlands.

The MAT and MR tests are used for determining the activity of the cracking catalyst prior to (MAT test) and after (MR test) contamination of the catalyst with metals (nickel and vanadium). The higher the rate constant k and the conversion, the more active the catalyst will be. The results mentioned in Table 2 illustrate the extraordinary effectiveness of catalysts containing a barium titanium oxide, in particular barium titanate.

The results also show that the amount of barium titanium oxide in the total catalyst composition can be varied within wide limits. For comparison, the table gives the test results obtained with additives that are known from the state of the art discussed hereinbefore.

TABLE 1

	Catalyst Composition and Properties								
	BaTiO ₃				BaTi ₃ O ₇	BaAcAc*	BaCO ₃	BaZrO ₃	GaTiO ₃
	2.5%	5%	10%	20%	8.5%	10%	20%	20%	20%
REHN ₄ Y-zeolite (%; SiO ₂ /Al ₂ O ₃ = 5)	15	15	15	15	15	15	15	15	15
Silica-alumina 97%/3%	20	20	20	20	20	20	20	20	20
Kaolin (%)	62.5	60	55	45	56.5	55	45	45	45
Na ₂ O (%)	0.23	0.28	0.28	0.26	0.26	0.24	0.25	0.23	0.24
RE ₂ O ₃ (%)	1.7	2.0	1.9	2.0	1.8	2.0	2.0	1.7	2.0
SA (m ² /g; fresh)	113	136	116	99	124	144	106	114	89
SA (m ² /g; 795° C.)	54	58	52	45	48	39	30	—	28
ABD (g/cal)	0.70	0.72	0.76	0.80	—	0.56	0.80	—	0.78

% = weight percentage
*Barium acetyl acetate

TABLE 2

	Test Results								
	BaTiO ₃				BaTi ₃ O ₇	BaAcAc	BaCO ₃	BaZrO ₃	CaTiO ₃
	2.5%	5%	10%	20%	8.5%	10%	20%	20%	20%
MAT - 795° C.-Test:									
k	16.9	17.2	16.1	15.0	15.2	13.2	10.2	11.6	9.4
Conversion %	58.5	58.7	57.0	55.3	55.7	52.2	46.0	49.2	44.0
Gas total %	11.2	10.9	10.5	10.3	10.9	9.2	8.4	8.5	7.5
Gasoline %	44.8	45.2	44.2	42.6	42.6	41.0	35.7	39.0	35.1
LCO %	23.6	23.6	23.3	23.8	23.7	23.3	24.4	23.3	23.4
Coke %	2.5	2.6	2.4	2.3	2.3	2.0	1.9	1.7	1.4
MR-Test:									
V (ppm)	3158	3201	3324	2971	3120	3238	3076	3270	3257
Ni (ppm)	952	1026	995	998	1085	1007	1016	954	860
k	19.8	24.2	22.2	21.5	18.4	9.6	20.4	17.1	14.9
Conversion %	62.1	66.7	64.7	64.2	60.4	44.1	62.8	58.8	55.1
Gas total %	12.6	13.6	13.6	13.7	12.4	7.0	11.9	12.7	10.4
Gasoline %	45.4	48.1	46.1	46.1	44.6	34.2	46.7	42.6	41.6
LCO %	22.5	20.6	21.3	21.6	22.2	25.1	21.0	21.7	23.2
Coke %	4.1	5.0	5.0	4.4	3.6	3.0	4.3	3.6	3.2
H ₂	0.13	0.12	0.13	0.12	0.15	0.24	0.14	0.09	0.16

EXAMPLE 2

Using the procedure described in Example 1, catalysts A and B were prepared that contain an ultrastable Y-zeolite and are further characterized by the composition and properties mentioned in the table below.

TABLE III

	Catalyst Composition and Properties	
	Catalyst A	Catalyst B
Ultrastable Y-zeolite (a ₀ = 24.53 Angstroms)	25	25
Kaolin (%)	55	35
Silica (%)	20	20
BaTiO ₃ (%)	0	20
RE ₂ O ₃ (%)	0	0
Na ₂ O (%)	0.16	0.28
SA (m ² /g; fresh)	232	259
SA (m ² /g; 795° C.)	132	129

The test results in the following Table IV show the excellent resistance to metal (see MR test) of catalyst B, which contains barium titanate.

TABLE IV

	Test Results	
	Catalyst A	Catalyst B
MAT - 795° C.-Test:		
k	12.8	13.3
Conversion	51.7	52.2
Gas total (%)	11.7	11.3
Gasoline (%)	38.4	39.6
LCO (%)	24.9	24.8
Coke (%)	1.6	1.7
MR-Test:		
V (ppm)	3350	3132
Ni (ppm)	1225	1045
k	3.7	15.8
Conversion (%)	32.3	56.9
Gas total (%)	5.8	13.2
Gasoline (%)	23.7	40.8
LCO (%)	26.6	24.2
Coke (%)	2.9	2.9
H ₂ (%)	0.65	0.36

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EXAMPLE 3

Using the procedure described in Example 1, the following Y-zeolite-containing "active" and barium titanate-containing "less active" catalyst particles were prepared.

TABLE V

Catalyst Composition		
	Active Particles	Less Active Particles
RENH ₄ -Y-zeolite (%)	30	0
Kaolin (%)	50	70
Silica (%)	20	20
BaTiO ₂ (%)	0	10

Then a mixture was prepared of equal amounts by weight of the two types of particles. The mixture contained 1.6 RE₂O₃, 0.25% Na₂O and had an SA=109 m²/g. The MAT and MR test results show the effectiveness of this cracking catalyst mixture.

TABLE VI

Test Results	
<u>MAT - 795° C.-Test</u>	
k	16.6
Conversion (%)	57.9
Gas total (%)	10.9
Gasoline (%)	44.4
LCO (%)	23.1
Coke (%)	2.6
<u>MR-Test</u>	
V (ppm)	3230
Ni (ppm)	935
k	16.7
Conversion (%)	58.2
Gas total (%)	11.8
Gasoline (%)	42.5
LCO (%)	22.8
Coke (%)	3.8
H ₂ ' (%)	0.19

What is claimed is:

1. A fluidized cracking catalyst comprising a zeolitic, crystalline aluminosilicate, a matrix material and a barium titanium oxide.

2. A catalyst according to claim 1, wherein said barium titanium oxide and said zeolitic, crystalline aluminosilicate are collectively incorporated in a matrix comprising said matrix material.

3. A catalyst according to claim 1, comprising 1 to 20 percent by weight of said barium titanium oxide.

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4. A catalyst according to claim 1, comprising 1 to 10 percent by weight of said barium titanium oxide.

5. A catalyst according to claim 4, comprising 10 to 30 percent by weight of said zeolitic, crystalline aluminosilicate.

6. A catalyst according to claim 5, wherein said barium titanium oxide and said zeolitic, crystalline aluminosilicate are embedded in 10 to 90 percent by weight of said matrix material.

7. A catalyst according to claim 1, wherein said barium titanium oxide is physically separated from said zeolitic, crystalline aluminosilicate, said catalyst comprising:

a. catalytically active particles comprising said zeolitic, crystalline embedded in said matrix material, and

b. catalytically less active particles comprising said barium titanium oxide embedded in said matrix material.

8. A catalyst according to claim 7, wherein said catalytically less active particles contain 10 to 40 percent by weight of barium titanium oxide.

9. A catalyst according to claim 8, wherein said catalytically active particles contain 20 to 40 percent by weight of said zeolitic, crystalline aluminosilicate.

10. A catalyst according to claim 1, wherein said barium titanium oxide is barium titanate.

11. A catalyst according to claim 1, further comprising a clay.

12. A catalyst according to claim 1, further comprising a passivator.

13. A catalyst according to claim 1, further comprising an oxidation promoting metal or metal compound.

14. Particles comprising barium titanium oxide embedded in a matrix material.

15. Particles according to claim 14, wherein said barium titanium oxide is barium titanate.

16. A catalyst according to claim 7, wherein said barium titanium oxide is barium titanate.

17. A catalyst according to claim 1, wherein said aluminosilicate is selected from the group consisting of zeolites A, X, Y, ultrastabilized sieves, ZK-4, ZK-5, ZSM-5, ZSM-11 and ZSM-12.

18. A catalyst according to claim 1, wherein said matrix material is selected from the group consisting of silica, silica-alumina, alumina, zirconia, titania, magnesia and mixtures thereof.

19. A catalyst according to claim 1, wherein the barium titanium oxide is selected from the group consisting of BaTiO₃, BaTi₃O₇, BaTi₄O₉, Ba₂TiO₄, Ba₂Ti₅O₁₂, Ba₂Ti₉O₂₀, Ba₄Ti₁₃O₃₀ and Ba₆Ti₁₇O₄₀.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : Re. 35,406
DATED : December 17, 1996
INVENTOR(S) : BARIUM TITANIUM OXIDE-CONTAINING FLUIDIZABLE
CRACKING CATALYST COMPOSITION

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col. 2, line 3, change "BaTi4O9" to --BaTi₄O₉--.

In Table 1, line 2, change "GaTiO₃" to --CaTiO₃--;

line 14, change "(g/cal)" to --(g/ml)--.

In Table IV, line 14, change "3.7" to --5.7--.

Claim 7, column 8, line 15, after "crystalline" insert
--aluminosilicate--.

Signed and Sealed this

Eighteenth Day of February, 1997

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks