

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(10) International Publication Number

WO 2019/147345 A1

(43) International Publication Date

01 August 2019 (01.08.2019)

(51) International Patent Classification:

CI0G 35/06 (2006.01)	B01J 37/00 (2006.01)
B01J 29/08 (2006.01)	B01J 29/89 (2006.01)

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/US2018/064001

(22) International Filing Date:

05 December 2018 (05.12.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15/877,788 23 January 2018 (23.01.2018) US

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(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(54) **Title:** MODIFIED USY-ZEOLITE CATALYST FOR REFORMING HYDROCARBONS

(57) **Abstract:** The invention relates to a reforming catalyst. The reforming catalyst comprises a reforming metal, such as Pt, a support, such as an alumina support, and a USY zeolite, which has had part of its aluminum framework substituted with Zr and Ti. The amount of USY zeolite does not exceed 5 wt%, and most preferably, contains 2 -3 wt% USY zeolite.

MODIFIED USY-ZEOLITE CATALYST FOR REFORMING HYDROCARBONS

FIELD OF THE INVENTION

[001] The present invention relates to a catalyst for catalytic reforming of hydrocarbon oil containing a framework-substituted zeolite-Y in which zirconium atoms and/or hafnium atoms and/or titanium atoms form a part of a framework of an ultra-stable Y-type zeolite.

BACKGROUND AND PRIOR ART

[002] Catalytic reforming is a major conversion process in petroleum refinery and petrochemical industries. The reforming process is a catalytic process which converts low octane naphtha that have been, e.g., distilled from crude oil, into higher octane reformate used in gasoline blending and aromatic rich reformates used for aromatic production. Basically, the process re-arranges or re-structures the hydrocarbon molecules in naphtha feedstocks and breaks some of the molecules into smaller molecules. Naphtha feeds to catalytic reforming include heavy straight run naphtha. It transforms low octane naphtha into high-octane motor gasoline blending stock and aromatics rich in benzene, toluene, and xylene with hydrogen and liquefied petroleum gas as a byproduct. With the fast growing demand in aromatics and demand of high-octane numbers, catalytic reforming is likely to remain one of the most important unit processes in the petroleum and petrochemical industry. There are various commercial catalytic reforming processes which will be well known to the skilled artisan.

[003] Given the importance of preparing useful products from crude oil, it is not surprising that there is a substantial literature on catalytic reforming processes.

[004] U.S. Patent No. 4,698,322 to Santilli teaches a reformation catalyst containing (i) Pt, (ii) type L zeolite, and (iii) a “promoter” which can be Fe, Co, or Ti. The ratio of Pt to promoter is less than 10:1. This “promoter” is not inserted into the zeolite framework which, in any event, differs from USY zeolite. No binder is disclosed either.

[005] U.S. Patent No. 5,271,761 to Skeels teaches zeolite Y molecular sieves. The artisan recognizes that, while USY and zeolite Y both have an FAU framework, they differ in composition and properties. The '761 Patent also describes mole fractions of TiO₂, AlO₂, and

SiO_2 , as well as Si/Ti ratios and $(\text{Si} + \text{Al})/\text{Ti}$ ratios, which are not within the ranges of those of the invention described herein.

[006] Also see U.S. Patent No. 5,690,810 to Lawrence, et al., teaching reforming processes using solid acids, Group III or Group IV members of the periodic table, and Group VIII metal deposits. Also see U.S. Patent No. 9,499,403 to Al-Muhaish, et al., U.S. Patent No. 8,008,226 and U.S. Patent No. 7,700,005 to Inui et al.

[007] U.S. Patent No. 9,512,371 describes incorporating Ti into FAU zeolites, followed by their use as hydrocracking catalysts. The weight % ratio of Al/Si ranges from 0.14 – 0.35, which is well outside of the range of the present invention.

[008] In a sense, catalytic hydrocracking may be viewed as the “opposite” of reforming processes, because in the former, large molecules are broken (“cracked”) into smaller ones, while reformation converts the molecules by, e.g., dehydrogenation, isomerization, alkylation, and cracking reactions converting starting materials into high octane containing molecules. Again, the literature on hydrocracking catalysts is enormous, and the inventors wish to draw attention to U.S. Patent No. 9,221,036, incorporated by reference in its entirety. The ‘036 patent teaches, *inter alia*, a hydrocracking catalyst in which a USY framework has been substituted, in part, by one or more of zirconium, titanium, and hafnium. In these catalysts, the metal (Ti , Zr , and/or Hf), substitutes for part of the aluminum in the aluminum/silica framework, and essentially become part of the framework. Processes for making these catalysts and their use, are all described in the ‘036 patent. Examples 1 and 2, *infra*, are in fact taken from this Patent.

[009] Zeolite based catalysts provide sufficient acidity to function in cracking, which are desirable in hydrocracking. In contrast, these reactions are very undesirable in reforming reactions, so a goal of developing any new reforming catalyst is a reduction of acidity in the catalytic composition.

[0010] Further, characteristic metals which are used in hydrocracking are Ni , Mo , and W , alone or preferably, in combination. Such metals are avoided in reforming catalysts, which are characterized by the presence of noble metals. A further fundamental difference is the

temperature at which hydrocracking and reforming reactions operate, with the latter type of reaction requiring temperatures of 500° C. or more, well above those used in hydrocracking.

[0011] Given the different aims, and reagents, used in reforming processes and hydrocracking, it is surprising that a hydrocracking catalyst can be modified to become a reforming catalyst. Yet, this is the subject of the invention, which is elaborated upon in the disclosure which follows.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0012] The invention includes a catalyst useful in reforming processes, wherein an ultra stable Y ("USY" hereafter) zeolite is framework substituted to incorporate one or more of zirconium, titanium, and hafnium into its framework, and also has impregnated therein a reforming process metal, such as Pt, Rh, or Pd. Optionally, the reforming catalyst can include or comprise a metal such as V, Zn, Ga, Li, Ca, Mg, or a rare earth metal.

[0013] The USY zeolite, base component of the catalysts of the invention contains from 0.1 to 5 mass % of one or more of Zr, Ti, and Hf, as calculated on their oxide basis. The reforming metal is present in an amount from 0.01 to 1 wt%, preferably from 0.1 to 0.4 wt% of the resulting catalyst composition. The amounts of the individual materials supplying Zr, Ti, and Hf is less than 0.1 wt%, but when combined, the total is at least 0.1 wt%.

[0014] *In toto*, the catalytic compositions comprise a binder, e.g., an alumina binder, a USY zeolite, and the aforementioned metals. The amount of USY-zeolite should not exceed 50 wt%, and is preferably 1-10, more preferably 1-5, and most preferably 2-3 wt% of the total composition.

EXAMPLES

EXAMPLE 1

[0015] Manufacture of An Ultra-Stable Y Zeolite

[0016] First, 50.0 kg of a NaY zeolite (hereinafter, also referred to as "NaY") having a SiO₂/Al₂O₃ molar ratio of 5.2, a unit cell dimension (UD) of 2.466 nm, a specific surface area

(SA) of 720 m²/g, and a Na₂O content of 13.0% by mass was suspended in 500 liter (hereinafter, also expressed as "L") of water having a temperature of 60° C. Then, 14.0 kg of ammonium sulfate was added thereto. The resulting suspension was stirred at 70° C. for 1 hour and filtered. The resulting solid was washed with water. Then the solid was washed with an ammonium sulfate solution of 14.0 kg of ammonium sulfate dissolved in 500 L of water having a temperature of 60° C., washed with 500 L of water having a temperature of 60° C., dried at 130° C. for 20 hours, thereby affording about 45 kg of a Y zeolite (NH₄⁶⁵Y) in which 65% of sodium (Na) contained in NaY was ion-exchanged with ammonium ion (NH₄⁺). The content of Na₂O in NH₄⁶⁵Y was 4.5% by mass.

[0017] NH₄⁶⁵Y 40 kg was fired in a saturated water vapor atmosphere at 670° C. for 1 hour to form a hydrogen-Y zeolite (HY). HY was suspended in 400 L of water having a temperature of 60° C. Then 49.0 kg of ammonium sulfate was added thereto. The resulting mixture was stirred at 90° C. for 1 hour and washed with 200 L of water having a temperature of 60° C. The mixture was then dried at 130° C. for 20 hours, thereby affording about 37 kg of a Y zeolite (NH₄⁹⁵Y) in which 95% of Na contained in the initial NaY was ion-exchanged with NH₄. NH₄⁹⁵Y 33.0 kg was fired in a saturated water vapor atmosphere at 650° C. for 1 hour, thereby affording about 15 kg of a ultra stable Y zeolite (hereinafter, also referred to as "USY (a)") having a SiO₂/Al₂O₃ molar ratio of 5.2 and a Na₂O content of 0.60% by mass.

[0018] Next, 26.0 kg of this USY (a) was suspended in 260 L of water having a temperature of 60° C. After 61.0 kg of 25% sulfuric acid by mass was gradually added to the suspension, the suspension was stirred at 70° C. for 1 hour. The suspension was filtered. The resulting solid was washed with 260 liter of deionized water having a temperature of 60° C. and dried at 130° C. for 20 hours, thereby affording a ultra stable Y-type zeolite (hereinafter, also referred to as "USY (b)").

[0019] USY (b) was fired at 600° C. for 1 hour, thereby affording about 17 kg of ultra stable Y-type zeolite (hereinafter, also referred to as "USY (c)").

EXAMPLE 2

[0020] 1 kg of USY (c) obtained in Example 1 was suspended in 10 L of water at 25° C., and the pH of the solution was adjusted to 1.6 by sulfuric acid of 25% by mass. Zirconium sulfate of 18% by mass (86 g) and titanyl sulfate of 33% by mass (60 g) were added and mixed, and the suspension was stirred at room temperature for 3 hours. Then, the pH was adjusted to 7.2 by adding 15% by mass aqueous ammonia, and the suspension was stirred at room temperature for 1 hour and then filtered. The product obtained was washed with 10 L of water and dried at 130° C. for 20 hours to obtain about 1 kg of a zirconium/titanium-substituted type zeolite (hereinafter referred to as "USY (E)"). Analysis showed the USY contained 0.8% by weight of TiO₂, and a total of 1.39% by weight of TiO₂ and ZrO₂.

EXAMPLE 3

[0021] This example presents a catalyst prepared in accordance with the invention.

[0022] A catalyst support was prepared by combining 95 wt% of an alumina binder as a support, and 5 wt% of a framework inserted Ti-Zr-USY prepared in accordance with Example 2, *supra*. This support was then impregnated with Pt, by mixing 600g of the support with a solution of tetra-amine Pt containing 1.9 wt% Pt. (This solution was prepared by dissolving 63g of tetra-amine platinum in water). This served to impregnate the catalyst support with Pt. The product was then air dried at 120° C. for one hour, and calcined at 400° C. for one hour. Analysis showed that 0.2 wt% Pt had been impregnated in the support.

[0023] Though not discussed in this Example, the mixture as prepared may be mixed with a catalyst support (e.g., alumina, silica, or mixes thereof, or any catalyst support known to the art) and then extruded, at room temperature prior to drying and calcination. The mixing and extrusion will be familiar to the skilled artisan, as well as by way of review of the '036 Patent, *supra*.

EXAMPLE 4

[0024] The catalyst prepared in Example 3, was used in a pilot study, which took place over sixteen (16) days. The conditions were changed, so as to determine the impact of various

parameters. The pilot plant was operated at 510° C., at a pressure range of 6-8 bars, a liquid hourly space velocity range of 1.0-1.5 h⁻¹ and a hydrogen to hydrocarbon ratio range of 3.5-5.0. Table 1 shows the composition of the test feedstock. Table 2 refers to the final results. “Feed” refers, of course, to the composition of the feedstock. “Commercial” refers to a commercially available catalyst compared to the catalyst of Example 3.

Table 1. Feedstock properties

Property (unit)	Unit	Value
Density @ 15°C	Kg/L	0.7374
API Gravity	°	60.2
Distillation		
IBP	°C	78
10W%	°C	100
30W%	°C	112
50W%	°C	125
70W%	°C	139
90W%	°C	156
FBP	°C	173
Paraffins	W%	70.8
Olefins	W%	1.6
Naphthenes	W%	14.5
Aromatics	W%	13.0
Sulfur	Ppmw	0.3

Table 2. Process performance.

Composition/Property	Unit	Feed	Commercial	EXAMPLE 3
Paraffin	W%	36.8	9.9	10.0
I-Paraffins	W%	34.0	18.4	16.1
Aromatics	W%	13.0	68.3	68.3
Naphthenes	W%	14.5	1.0	1.3
Olefins	W%	1.6	2.4	4.3
Calculated RON		38.9	97.4	97.1
Avg MW	Kg/Kmol	109.6	97.3	97.1
Mass Balance	W%		93	101
Liquid Yield	W%		74	68
H2 Yield	W%		0.65	0.52

[0025] The foregoing examples set forth embodiments of the invention, which include a reforming catalyst, a process for making the reforming catalyst, and its use.

[0026] The reforming catalyst of the invention is a composition comprising an ultra stable (“US”) Y type zeolite, with a framework in which part of the aluminum has been substituted with Zr and Ti, and to which a reforming metal has been added. The reforming metal is preferably added in an amount of from 0.01-1.0 wt% of the total weight of catalyst. “Reforming metals” as used herein includes the noble metals, i.e., Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au, with Pt and Pd being preferred. Optionally, the framework of the zeolite may contain one or more of V, Zn, Ga, Li, Ca, Mg, and the rare earth elements.

[0027] The actual amount of USY-zeolite in the catalyst is less than 50% by weight, but is preferably as low as 1-10 wt%, preferably 1-5 wt%, most preferably 2-3 wt%. As in the ‘036 Patent, the Zr, Ti, Hf and other optional metals used, may be present in amounts ranging from 0.1-5% by mass of the zeolite base component. Other characteristics of the zeolite of the reforming catalyst include a crystal lattice constant of from 2.425 to 2.450 nm, preferably 2.430-2.450 nm, a specific surface area of from 600 m²/g to 900 m²/g, and a molar ratio of SiO₂ to Al₂O₃, generally ranging from 5:1 to 100:1 and preferably from 20:1 to 100:1. These reforming catalysts preferably have a specific surface area of from 200 to 450 m²/g, and a pore volume of from 0.4 – 1.00 ml/g.

[0028] The catalytic composition of the zeolite component, in preferred embodiments, contains from 0.25 to 1.25 wt% of TiO₂. Preferably, it contains from 0.75 to 1.0 wt% TiO₂, and most preferably, 0.8 wt% TiO₂ (which corresponds to 0.01 mol% of TiO₂).

[0029] The catalysts of the invention are made, essentially, by using the processes described in U.S. Patent No. 9,221,036, incorporated by reference *supra*, via, the USY zeolite of Example 2 is placed in suspension, preferably to form a suspension having a liquid/solid mass ratio of from 5 to 15, after which an acid is preferably added to bring the suspension to a pH of from 1 to 2, after which Zr and Ti are added and mixed, followed by neutralization. The resulting material is combined with a binder, such as an alumina binder, and impregnated with a noble metal by adding a solution of the noble metal thereto, followed by drying and calcining.

[0030] In use, the reforming catalyst of the invention is contacted to a hydrocarbon feedstock having a boiling point in the range of 36 – 250° C., at a reaction temperature of from 400° C. to 600° C., preferably 430° C. – 600° C., and most preferably 430-550° C., and a

pressure of from 1 bar to 50 bars, an LHSV of from 0.5 to 5 h⁻¹, and a hydrogen to hydrocarbon feed ratio of from 1:1 to 50:1, preferably 1:1 to 30:1. Various methods may be used, such as a fixed bed reactor, a catalyst replacement reactor, a semi-regenerative fixed bed reactor, a cyclic fixed bed reformer, or a continuous reformer.

[0031] Other features of the invention will be clear to the skilled artisan and need not be reiterated here.

[0032] The terms and expression which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expression of excluding any equivalents of the features shown and described or portions thereof, it being recognized that various modifications are possible within the scope of the invention.

We Claim:

1. A reforming catalyst comprising a reforming metal carried on a support containing an ultra-stable (US) Y-type zeolite, in which a portion of aluminum atoms of the framework of said USY zeolite thereof is substituted with one or more of zirconium, titanium and hafnium atoms.
2. The reforming catalyst for hydrocarbon oil according to claim 1, wherein said zeolite-1 contains from 0.1 to 5 mass% of zirconium atoms and titanium atoms as calculated on an oxide basis.
3. The reforming catalyst according to claim 1, wherein the said support is an alumina or a silica-alumina support.
4. The zeolite of the reforming catalyst according to claim 1, wherein said reforming catalyst has:
 - (a) a crystal lattice constant of 2.425 to 2.450 nm,
 - (b) a specific surface area of 600 to 900 m²/g, and
 - (c) a molar ratio of SiO₂ to Al₂O₃ of 5 to 100.
5. The reforming catalyst according to claim 1, having a specific surface area of from 200 to 450 m²/g; and a pore volume of from 0.40 to 1.00 ml/g.
6. The reforming catalyst of claim 1, comprising from 0.01 – 1.0 wt% of reforming metals.
7. The reforming catalyst of claim 1, wherein said reforming metal comprises a noble metal.
8. The reforming catalyst of claim 7, wherein said noble metal is Ru, Rh, Pd, Ag, Os, Ir, Pt, or Au.
9. The reforming catalyst of claim 8, wherein said noble metal is Pt.
10. The reforming catalyst of claim 1, comprising less than 50 wt% USY zeolite.
11. The reforming catalyst of claim 10, comprising 1-10 wt% USY zeolite.

12. The reforming catalyst of claim 1, comprising 1-5 wt% USY zeolite.
13. The reforming catalyst of claim 1, wherein said Y-type zeolite comprises V, Zn, Ga, Li, Ca, Mg, or a rare earth metal.
14. A method for reforming a hydrocarbon feedstock comprising contacting said feedstock with the reforming catalyst of claim 1, at a reaction temperature of from 430° C. to 600° C., a pressure of from 1 to 50 bars, an LHSV of from 0.5 to 5 h⁻¹, and a hydrogen feedstock ratio of from 1:1 to 50:1.
15. The method of claim 14, wherein said reaction temperature is from 430° C. to 550° C.
16. The method of claim 14, wherein said hydrogen feedstock ratio ranges from 1:1 to 30:1.
17. The method of claim 14, comprising reforming said feedstock in a fixed bed reactor.
18. The method of claim 17, wherein said fixed bed reactor is a semi-regenerative fixed bed reactor.
19. The method of claim 14, comprising reforming said hydrocarbon feedstock in a cyclic fixed bed reformer.
20. The method of claim 14, comprising reforming said hydrocarbon feedstock in a continuous reformer.
21. The method of claim 17, comprising reforming said catalyst in a catalyst replacement reactor.
22. The method of claim 14, wherein said feedstock has a boiling point of from 36-250° C.
23. A process for making the reforming catalyst of claim 1, comprising forming a suspension of USY type zeolite in which a portion of aluminum atoms in the framework of said USY type zeolite has been substituted with zirconium and titanium atoms and/or hafnium, a binder, and a reforming metal.
24. The process of claim 23, wherein said reforming metal is Pt.

25. The process of claim 23, wherein said USY zeolite containing catalyst is present in an amount less than 50 wt%.
26. The process of claim 25, wherein said USY zeolite containing catalyst is present in an amount of 5-10 wt%.
27. The process of claim 25, wherein said USY zeolite containing catalyst is present in an amount of 1-5 wt%.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/064001

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10G35/06 B01J29/08 B01J37/00 B01J29/89
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier application or patent but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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Date of the actual completion of the international search	Date of mailing of the international search report
18 February 2019	27/02/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Ruiz Martínez, C

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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