



(51) International Patent Classification:

B01J 29/12 (2006.01) **C07C 5/41** (2006.01)
B01J 37/10 (2006.01) **C10G 35/095** (2006.01)

(21) International Application Number:

PCT/US2012/055896

(22) International Filing Date:

18 September 2012 (18.09.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/235,858 19 September 2011 (19.09.2011) US

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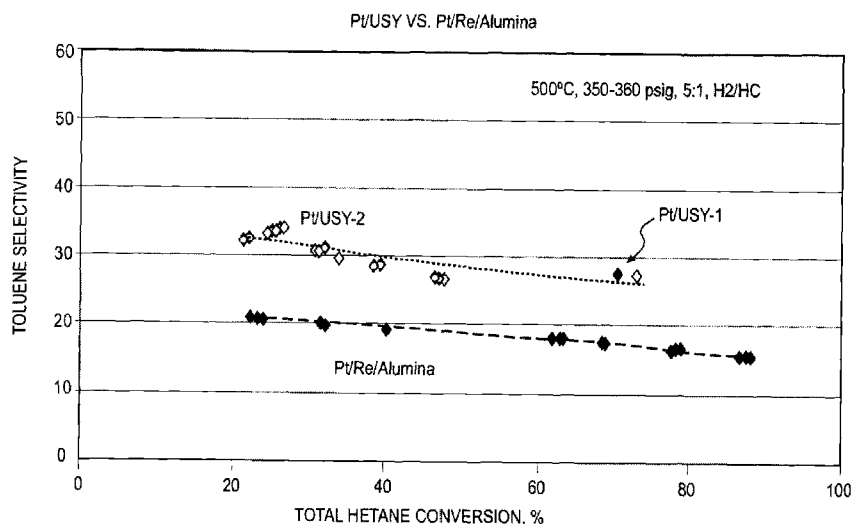
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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.

(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, 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, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: REFORMING CATALYST COMPOSITIONS



(57) Abstract: Process for the preparation of a catalyst suitable for use in a naphtha reforming process, the process including providing a Y zeolite with an initial SiO₂:Al₂O₃ molar ratio of at least 150, introducing the Y zeolite to a binder to form an intermediate composition, extruding the intermediate composition, reducing the alpha acidity of the extruded composition to provide a low acid composition, and introducing a noble metal to the low acid composition. Processes and systems of converting naphtha to a higher-octane hydrocarbon supply using catalysts, as prepared herein, are also disclosed.

REFORMING CATALYST COMPOSITIONS

FIELD

[0001] The presently disclosed subject matter relates to catalyst compositions that are chlorine free and more stable. These catalyst compositions permit longer cycles with less regeneration cycles and reduce maintenance costs from downstream corrosion associated with standard chlorine containing catalysts. The catalyst compositions in accordance with the presently disclosed subject matter can increase the octane rating of a naphtha feed, which in turn can be blended with, for example gasoline to provide a high-octane gasoline and other fuel products. Furthermore, the catalyst compositions in accordance with the presently disclosed subject matter can increase gasoline yield at the same octane level or increase octane level at the same yield.

BACKGROUND

[0002] Catalytic reforming of naphtha is widely used in the petroleum refining industry to increase the octane of naphtha for gasoline blending. Important reactions that occur in catalytic reforming include 1) the dehydrogenation of naphthenes to aromatics, 2) isomerization of paraffins to isoparaffins, and 3) the dehydrocyclization of paraffins to aromatics.

[0003] Undesirable reactions include the hydrocracking of paraffins and naphthenes and the dealkylation of aromatics that results in the loss of liquid and hydrogen yields and the production of lower-valued fuel gas. A more selective reforming catalyst could significantly increase reforming margins by increasing liquid and hydrogen yields via reduced hydrocracking and increased paraffin dehydrocyclization activity.

[0004] Dual functional reforming catalysts have been commercialized. Early reforming catalysts consisted of platinum metal supported on an acidic, chlorided alumina. Chlorine is typically added to the reforming catalyst to maintain the acidity. The chlorine needs to be replenished and presents operating issues. Chlorine is corrosive to the unit and highly reactive. Their key limitation was coke stability. Bimetallic reforming catalysts (PtRe/Al₂O₃) have been introduced with improved stability and provided equivalent activity and selectivity to earlier catalysts. PtIr/Al₂O₃ catalysts have also been commercialized that are higher activity but less selective than Pt and PtRe

catalysts. Other reforming catalyst, such as PtSn, seek to provide higher stability for improved operation at lower pressure. However, there remains a need for reforming catalyst with improved selectivity and/or that provide an increase in gasoline yield.

SUMMARY

[0005] One aspect of the presently disclosed subject matter provides a process for the preparation of a catalyst suitable for use in a naphtha reforming process. The process includes providing a Y zeolite with an initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of at least 150, introducing the Y zeolite to a binder to form an intermediate composition, extruding the intermediate composition, reducing the acidity of the extruded composition to provide a low acid an acidity-reduced composition, and introducing a noble metal to the low acid composition. The low acid composition has a reduced number of Bronsted acid sites compared to a similar composition without reduced acidity. The catalyst prepared according to the presently disclosed process is improved because it is chlorine free, which provides numerous advantages. The catalyst is more stable. The catalyst is capable of operating (i) with longer cycle times at the same temperature and pressure resulting in less down time normally associated with catalyst regeneration or (ii) at higher temperatures and/or higher pressures with the same cycle time. Operating at higher temperatures results in a product with higher octane. Operating at higher pressures results in improved product yield.

[0006] The chlorine free catalyst produced in accordance with the presently disclosed subject matter provides additional benefits to the processing units. The presence of chlorine creates various operating issues, which require regular shutdowns for cleaning and repair. The use of the chlorine free catalyst reduces the corrosive environment with the processing unit, which reduces corrosion issues. The catalyst is less sensitive to water, which makes it better suited for use in facilities in humid environments. A further benefit is the reduction in coke production when compared to the use of a chlorine containing catalyst. The coke formation is greatly reduced (i.e., coke level is an order of magnitude lower).

[0007] Another aspect of the presently disclosed subject matter provides a process for converting naphtha to a higher-octane hydrocarbon supply. The process includes providing a source of naphtha, and exposing the naphtha to a catalyst to convert the

naphtha to a higher-octane hydrocarbon supply. The catalyst can be any one of the catalyst compositions of the presently disclosed subject matter. In one embodiment, the catalyst is prepared by a process that includes providing a Y zeolite with an initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of at least 150, introducing the Y zeolite to a binder to form an intermediate composition, extruding the intermediate composition, reducing the acidity of the extruded composition to provide a low acid composition, and introducing a noble metal to the low acid composition.

[0008] Yet another aspect of the presently disclosed subject matter provides a system for converting naphtha to either (i) a higher-octane hydrocarbon supply at the same yield or (ii) a higher supply of hydrocarbon at the same octane. The system includes a source of naphtha, at least one vessel having an inlet to receive at least a portion of the naphtha and an outlet to discharge a stream of converted naphtha and a catalyst housed in the vessel to convert the naphtha to a higher octane hydrocarbon. The catalyst can be any one of the catalyst compositions of the presently disclosed subject matter. In one embodiment, the catalyst is prepared by a process that includes providing a Y zeolite with an initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of at least 150, introducing the Y zeolite to a binder to form an intermediate composition, extruding the intermediate composition, reducing the acidity of the extruded composition to provide a low acid composition, and introducing a noble metal to the low acid composition.

[0009] These and other features of the presently disclosed subject matter will become apparent from the following detailed description of embodiments which, taken in conjunction with the accompanying drawings, illustrate by way of example the principles of the present application.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The disclosed subject matter will now be described in conjunction with the accompanying drawings in which:

[0011] **Figure 1** depicts a schematic of an exemplary catalytic reforming process disclosed in U.S. Reissue Patent No. 33,323.

[0012] **Figure 2** is a plot of toluene selectivity vs. total heptane conversion, as described in Example 2.

[0013] **Figure 3** is a plot of gasoline yield v. gasoline research octane numbers (RON) for catalysts of the present application, as described in Example 3.

[0014] **Figure 4** is a plot of the temperature required for 95 RON vs. time on stream for catalysts of the present application, as described in Example 4.

[0015] **Figure 5** is a plot of the wt% hydrogen produced at 95 RON vs. time on stream, as described in Example 5.

DETAILED DESCRIPTION

Definitions

[0016] The term “alpha acidity” is known to those of ordinary skill in the art. As used herein, “alpha acidity” is defined as described in U.S. Patent No. 3,354,078, in the *Journal of Catalysis*, Vol. 6, pp. 522-529 (August 1965) and in the *Journal of Catalysis*, Vol 61, p. 395 (1980), each incorporated herein by reference. The alpha acidity is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and it gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). Generally, alpha acidity is based on the activity a highly-active silica-alumina zeolite cracking catalyst taken as an alpha of 1 (Rate constant = 0.016 sec^{-1}).

[0017] As used herein, the term “produced in an industrial scale” refers to a production scheme in which, for example, gasoline or other end product is produced on a continuous basis (with the exception of necessary outages for plant maintenance) over an extended period of time (e.g., over at least a week, or a month, or a year) with the expectation of generating revenues from the sale or distribution of the end product. Production at an

industrial scale is distinguished from laboratory or pilot plant settings which are typically maintained only for the limited period of the experiment or investigation, and are conducted for research purposes and not with the expectation of generating revenue from the sale or distribution of the end product produced thereby. In one embodiment, the catalysts of the present application are used to produce high-octane gasoline in an industrial scale.

[0018] Reference will now be made to various aspects of the present application in view of the definitions above.

[0019] In accordance with an initial aspect of the presently disclosed subject matter, a process is provided for the preparation of a catalyst suitable for use in a naphtha reforming process. The process includes providing a Y zeolite with an initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of at least 150, introducing the Y zeolite to a binder to form an intermediate composition, extruding the intermediate composition, reducing the alpha acidity of the extruded composition to provide an acidity-reduced composition, and introducing a noble metal to the acidity-reduced composition.

[0020] For purpose of illustration and not limitation, the initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio can be at least 175 or higher, for example, at least 200, or at least 225 or at least 250, or at least 255. The surface area of the Y zeolite can be at least $600 \text{ m}^2/\text{g}$, or alternatively at least $700 \text{ m}^2/\text{g}$, or still alternatively at least $750 \text{ m}^2/\text{g}$. The Y zeolite is typically in the H-form.

[0021] The binder can include SiO_2 , such as, for example, commercially available SiO_2 binders from Ultrasil Corporation and commercially available silica resin binders from Dow Corning. The SiO_2 binder can be added to the intermediate composition in an amount such the intermediate composition has a solid weight ratio of Y zeolite:binder of from about 7:3 to about 9:1 (e.g., 8:2) prior to being extruded, based on the total solid weight of the intermediate composition at 1000°F .

[0022] The extruded composition can be treated in one or more operations (e.g., a series of operations) that further reduce alumina induced acidity of the composition. After the performing the one or more operations to provide an acidity-reduced composition, the alpha acidity of the composition can be, for example, less than 1.25, or less than 1.0, or less than 0.75, less than 0.5, less than 0.4, less than 0.3, or less than 0.2. Common

techniques can be used to reduce the number of acid sites including, but not limited to streaming. These one or more operations can also impart and favor the formation of highly specific acid sites that help establish the high selectivity towards aromatics.

[0023] For example, the extrude composition can be calcined, such as, for example, a calcining operation in which the calcining occurs at a heat up rate of from about 3°F to about 7°F per minute. The extruded composition can be maintained, for example, at at least about 1000°F for at least 2 hours.

[0024] Alternatively, or in addition, the intermediate composition can be subjected to an ammonium exchange operation. According to one non-limiting embodiment, the pH of the extruded composition at beginning of the ammonium exchange operation can be from about 5.7 to about 5.0, and/or the pH of the extruded composition at the end of the ammonium exchange operation can be from about 4.5 to about 3.8. The ammonium exchange operation can include introducing a NH_4^+ source to a vessel (e.g., an exchange burette) that contains the extruded composition to mix the NH_4^+ source with the extruded composition.

[0025] Alternatively, or in addition, the intermediate composition can be subjected to a steaming operation. According to one non-limiting embodiment, the steaming operation includes heating the extruded composition to at least 1400°F at a rate of from about 3°F to about 7°F per minute and subsequently introducing steam to the heated composition.

[0026] Upon obtaining the low acid composition, a noble metal can be introduced. In one embodiment, the noble metal is selected from platinum, rhenium, iridium and combinations thereof. Furthermore, it is contemplated that any metal used for reforming catalysts are suitable. The noble metal can be introduced, for example, by a procedure in which the catalyst composition is introduced to an impregnation cone and rotated, and the noble metal is added to the rotating cone. According to a non-limiting embodiment, the noble metal can be added in an amount such that the final catalyst composition, prior to any additional drying or calcining operations, contains up to about 0.5 wt%, or up to about 0.7 wt%, or up to about 0.9 wt%, based on the total weight of the composition. Upon adding the noble metal, the composition can be subjected to a drying and/or calcining procedure. The resulting catalyst is substantially chlorine free.

[0027] Yet another aspect of the presently disclosed subject matter provides a process

for converting naphtha to a higher-octane hydrocarbon supply. The process includes providing a source of naphtha, and exposing the naphtha to a catalyst to convert the naphtha to a higher-octane hydrocarbon supply. The catalyst is prepared by a process that includes providing a Y zeolite with an initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of at least 150, introducing the Y zeolite to a binder to form an intermediate composition, extruding the intermediate composition, reducing the acidity of the extruded composition to provide a low acid composition, and introducing a noble metal to the low acid composition. The higher-octane hydrocarbon supply can be blended with, for example, gasoline to provide high-octane gasoline.

[0028] Yet another aspect of the presently disclosed subject matter provides a system for converting naphtha to a higher-octane hydrocarbon supply. The system includes a source of naphtha, at least one vessel having an inlet to receive at least a portion of the naphtha and an outlet to discharge a stream of converted naphtha and a catalyst housed in the vessel to convert the naphtha to a higher octane hydrocarbon. The catalyst can be any one of the catalyst compositions of the presently disclosed subject matter. The catalyst is prepared by a process that includes providing a Y zeolite with an initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of at least 150, introducing the Y zeolite to a binder to form an intermediate composition, extruding the intermediate composition, reducing the acidity of the extruded composition to provide a low acid composition, and introducing a noble metal to the low acid composition.

[0029] As noted above, the presently disclosed catalyst compositions are suitable for use in any naphtha reforming process. An exemplary, non-limiting reforming process is depicted in Figure 1, also disclosed in Reissue Patent No. 33,323 which is hereby incorporated by reference in its entirety. It is also contemplated that the presently disclosed catalyst compositions are suitable for use in the formation of aromatics with lower cetane numbers.

[0030] As disclosed in Re. 33,323, a full boiling range naphtha feedstream, comprising a range of hydrocarbons from C_3 to those boiling up to about 350°F and containing paraffins, naphthenes and aromatics is fed into distillation tower 1 to separate a C_5 - fraction from a C_{6+} fraction. The resultant C_{6+} fraction contains C_5 hydrocarbons, C_{10+} hydrocarbons, C_6 hydrocarbons and C_7 to C_9 hydrocarbons, while the C_5 - fraction contains C_6 hydrocarbons and C_{5-} hydrocarbons.

[0031] The C₆₊ fraction from distillation tower 1 is then fed into distillation tower 2 to separate a C₆ fraction from a C₇₊ fraction. The resultant C₆ fraction contains C₅ hydrocarbons, C₆ hydrocarbons and C₇₊ hydrocarbons, with the C₇₊ fraction containing C₆ hydrocarbons, C₇ to C₉ hydrocarbons and C₁₀₊ hydrocarbons.

[0032] The C₆ fraction is fed into the aromatizer reactor 3 which can contain a catalyst of the present application. The effluent from the aromatizer reactor 3 contains benzene, and toluene. The effluents are then fed into a flash drum 4 to separate a C₅₊ effluent with benzene being recovered in the flash drum. The C₄ stream containing hydrogen from the flash drum 4 is then recycled as needed to the aromatizer reactor 3 with excess used as make gas. The C₅₊ effluent is then fed into a stabilizer 5 to further purify and remove any C₄ hydrocarbons.

[0033] The C₇₊ fraction is fed into a conventional reformer 6 which can also contain a catalyst of the present application. The reformer effluent contains C₅ hydrocarbons, benzene, other C₆ hydrocarbons (excluding benzene), toluene, xylenes and C₉₊ hydrocarbons. The reformer effluent is then fed into a toluene rejection tower 7 from which a C₇ effluent containing C₇ hydrocarbon (mostly toluene) is taken as a sidestream, a C₆ effluent containing C₅ hydrocarbons, benzene, other C₆ hydrocarbons (excluding benzene) and C₇ hydrocarbons is taken overhead and a C₈₊ effluent containing C₇ and C₈ hydrocarbons (mostly xylenes) and C₉₊ hydrocarbons (mostly aromatics) is taken from the bottom. The C₈₊ effluent is then further distilled in a C₈/C₉ splitter tower 8 from which a C₈ effluent containing C₈ hydrocarbons and C₉₊ and a C₉₊ effluent containing C₈ hydrocarbons and mostly C₉₊ hydrocarbons is recovered.

[0034] The C₅₊ effluent from the aromatizer and the C₆ effluent and C₈ effluent from the reformer are then mixed and fed into the extraction unit 9 which utilizes sulfolane to solvent extract aromatics with the aromatics extract stream containing benzene, toluene and C₈ aromatics while the non-aromatic raffinate stream contains aromatics. The non-aromatic raffinate stream is then advantageously feed back to tower 2 to produce benzene. In connection with the production of benzene, the reforming catalysts in accordance with the presently disclosed subject matter may be employed in reactor 3 and reactor 6.

* * *

Example

[0035] The present application is further described by means of the examples, presented below. The use of such examples is illustrative only and in no way limits the scope and meaning of the presently disclosed subject matter or of any exemplified term. Likewise, the disclosed subject matter is not limited to any particular preferred embodiments described herein. Indeed, many modifications and variations of the disclosed subject matter will be apparent to those skilled in the art upon reading this specification. The disclosed subject matter is to be limited only by the terms of the appended claims along with the full scope of equivalents to which the claims are entitled.

Example 1 - Catalyst Support Preparation

[0036] The starting crystal was Tosoh390 HUA, obtained from Tosoh USA Inc. (Grove City, OH). The analysis of this crystal is shown in Table 1.

SiO ₂	97.52 wt%
Al ₂ O ₃	0.624 wt%
Na : 0.0036 wt%	0.0036 wt%
SiO ₂ :Al ₂ O ₃	266 molar ratio
Solids @ 1000°F	98.45 wt%
BET	808 m ² /gm
Alpha Acidity	1.4

Table 1. Starting Crystal Properties

Extrusion

[0037] During the mulling, a mixture of 806 gm of Tosoh390 HUA, 216 gm Ultrasil SiO₂ binder (Hayward, CA), 30 of Polyvinylalcohol and 900 gm deionized water were mixed and mulled in the Eirich mixer until an extrudeable mixture was obtained. The mixture was such as to obtain a 80/20 1000°F solids w/w ratio of USY(Tosoh390)/SiO₂(Ultrasil). USY is an ultrastabilized Y zeolite. The Eirich mixer employed in this non-limiting example is a tilted rotating pan of approximately 12" in diameter and a 6" height and can be obtained from Elrich Machines Inc. (Gurnee, IL). Internally, this mixer has rotating blades that were kept at the high RPM setting. The mixture was transformed from initially a powder consistency to a ~ 1/16"-1/8" spheroids consistency. This mixture was then extruded into 1/16" cylinders using a 2" diameter Bonnot extruder (Union Town, OH) to form a mulmix solid. The mulmix solids at

1000°F were 50.2 wt% (i.e., the amount of solid remaining). The crush strength of a small sample using an anvil of the extrudates after calcination at 1000°F were measured at 15.3 lbs/inch. The extrudates were dried overnight at 250°F in a drying oven.

Calcination

[0038] Material from the extrusion operation was then charged to a fixed bed calcining oven with air flowing upwards through the bed. The heat up rate was set at 5°F/min and the air rate was set at 10 Liter/min. When 1000°F was reached, the composition was maintained at 1000°F for 3 hours whereupon it was allowed to cool down to room temperature. The properties of the calcined support are given in Table 2.

BET	662 m ² /gm
Na	1210 ppm
Alpha acidity	0.1
UCS (Å)	24.29
nC ₆ Ads. Cap.	14.9 wt%

Table 2: Properties of calcined support

Ammonium Exchange

[0039] 1000 cc of the calcinated sample described in Table 2 were then loaded into a exchange burette and 5 Liters of 1N NH₄NO₃ are pumped around in up flow through the bed for 1hr. The pH at the start was 5.42 and the pH at the end was 3.85.

[0040] This step was repeated an additional 3 times. The start to finish pH values were 1) from 5.40 to 3.90; 2) from 5.32 to 4.25 ; and 3) from 5.33 to 4.35. Between each of these steps, the catalyst was washed with deionized water which results, interalia, in an increase in pH. After these exchanges, the catalyst was washed with 10 Liters deionized water and dried overnight at 250°F. Thereafter the support was calcined in air at 1000°F for 1hr using an initial heat up rate of 5°F/min with an air flow rate of 5 Liter/min. The product properties are shown in Table 3.

Na	255ppm
BET	670 m ² /gm
Alpha acidity	0.3
UCS (Å)	24.29
nC ₆ ads. Cap	17.3 wt%

Table 3: Properties of Ammonium-Exchanged Composition**Steaming**

[0041] 1000cc of the ammonium-exchanged composition described in Table 3 were charged to the steamer. Nitrogen flow was established at 5 L/min and the catalyst was ramped at 5°F/min until 1500°F was reached. At 1500°F, the flow was switched from N₂ to steam and held at 1500°F in 100% steam for 1hr. After this time, the earlier N₂ flow was re-established and steam was cut out and the catalyst was allowed to cool down. The product properties are shown in Table 4.

BET	628 m ² /gm
Alpha acidity	0.5
UCS (Å)	24.29
nC ₆ ads. Cap	13.7 wt%
Crush (lbs/inch)	58.2

Table 4: Properties of steamed support**Introduction of Noble Metal****Catalyst A - 0.9%Pt/Tosoh USY-1**

[0042] 11 gm of the steamed support described in Table 4 were charged to an impregnation cone and set to rotate at 20 RPM. The absorption capacity (AF value) was determined at 1.09 gm deionized water/gm support. 0.11 gm of Pt metal were added as 2.82 gms of a solution containing 3.904 wt% Pt and diluted with deionized water until 12 cc of impregnation volume were obtained. The Pt compound used in this non-limiting example was Pt-tetraamine-nitrate. Thereafter the pH of the solution was adjusted to 9.0. This solution was then sprayed onto the rotating support for approximately 15 minutes. When the spraying was finished, the batch was tumbled for an additional 30 min at 5 RPM. The impregnated catalyst was discharged and dried overnight at 250°F. The dried catalyst was then calcined for 1hr at 680°F in dry air at a flow rate of 5 vol air/vol catalyst/min and a heatup rate of 5°F/min was employed. The product properties are shown in Table 5.

Pt	0.93wt%
BET	621m ² /gm
H/Pt	0.55
UCS (Å)	24.29
nC ₆ ads. Cap.	15.0 wt%

Table 5: Properties of catalyst 0.9%Pt/Tosoh USY-1 (Catalyst A)

Catalyst B - 0.9%Pt/Tosoh USY-2

[0043] 11 gm of the steamed support described in Table 4 were charged were charged to an impregnation cone and set to rotate at 20 RPM. The absorption capacity (AF value) was determined at 1.09gm DI water/gm support. An amount of 0.11 gm of Pt metal were added as 2.82 gms of a vendor solution containing 3.904wt% Pt and diluted with DI water until 12 cc of impregnation volume were obtained. The Pt compound used in this non-limiting embodiment was Pt-tetraamine-nitrate. Thereafter the pH of the solution was adjusted to 8.5. This solution was then sprayed onto the rotating support in approximately 15 minutes. When the spraying was finished, the batch was tumbled for an additional 30 min at 5RPM. The impregnated catalyst was discharged and dried overnight at 250F. The dried catalyst was then calcined for 1hr at 680°F in dry air at a flow rate of 5vol air/vol catalyst/min and a heatup rate of 5°F/min was employed. The product properties are shown in Table 6.

Pt	0.92wt%
BET	615m ² /gm
H/Pt	0.58
UCS (Å)	24.29
nC ₆ ads. Cap.	15.2 wt%

Table 6: Properties of catalyst 0.9%Pt/Tosoh USY-2 (Catalyst B)

Catalyst A and Catalyst B have different adjusted pHs (e.g., 8.5 v. 9.0)/

Catalyst C (Comparative Example)

[0044] This alumina catalyst contained 0.9 wt% Cl and 0.09 wt% S, and is coated with 0.3% Pt/0.3%Re. Catalyst C (e.g., KX-120 catalyst) is a conventional reforming catalyst.

Catalyst D (Comparative Example)

[0045] This catalyst contained 0.3 wt% Pt, 0.8 wt% Cl and 0.04 wt% S. Catalyst D is a commercially available catalyst (e.g., Criterion PHF-43 (0.3 wt% Pt on Al₂O₃)).

Example 2 - Catalyst Testing Using a n-Heptane Feed

Test A (0.8 g catalyst at 500°C, 350 psig, 10 WHSV, and 5:1 H₂/HC)

[0046] The catalyst for testing (0.800 g, sized to 14-30 mesh) was diluted to 3 cc with 40-60 mesh quartz-chips and mixed. The well-mixed mixture was loaded to the middle zone of an isothermal, down-flow, fixed-bed, 3/8" outside diameter stainless steel reactor. After pressure test at 450 psig, the reactor pressure was set at 100 psig and H₂ flow was set at 200 cc/min. The reactor was heated at a ramp rate of 2°C/min from 20°C to 450°C, then at 5°C/min from 450°C to 500°C. After 30 minutes, the reactor was cooled down to 400°C. The reactor pressure was set at 350 psig. Once reaching 350 psig, the H₂ flow rate was reduced to 170 cc/min, and n-heptane was introduced to the reactor at 12 cc/hr. The reactor was heated at a ramp rate of 5°C/min from 400°C to 500°C. Fifteen minutes after the reactor reached 500°C, product analysis was conducted by an on-line GC (60M DB-1, -20°C, 2 min, 8°C/min to 250°C, hold for 30 min). The analysis continued every hour until a total of 6 GC analyses were conducted. The average data from GC2 to GC6 are reported in the data table.

Test B (0.19 g catalyst at 500°C, 350 psig, 16-50 WHSV, and 5:1 H₂/HC)

[0047] The catalyst for testing (0.19g, sized to 14-30 mesh) was diluted to 3 cc with 40-60 mesh quartz-chips. The same procedure described in Test A was followed to start the run. N-heptane and H₂ flow rates were set sequentially as shown below. Six GC analyses (once every hour) were conducted at each setting. The average data from GC2 to GC6 at each flow setting are reported in Table 7:

n-Heptane Rate Flow, cc/hr	14.0	9.0	6.2	4.5	14
H ₂ Rate, cc/min	198	127	88	66	198
n-Heptane WHSV	50	32	22	16	50

Table 7**Test C (0.8 g catalyst at 500°C, 350 psig, 4.8 - 12 WHSV, and 5:1 H₂/HC)**

[0048] The catalyst for testing (0.8 g, sized to 14-30 mesh) was diluted to 3 cc with 40-60 mesh quartz-chips. The same procedure described in Test A was followed to start the run. N-heptane and H₂ flow rates were set sequentially as shown below. Six GC analyses (once every hour) were conducted at each setting. The average data from GC2 to GC6 at each flow setting are reported in Table 8.

n-Heptane Flow Rate, cc/hr	14.0	11.8	8.4	5.6
H ₂ Flow Rate, cc/min	198	166	119	79.
n-Heptane WHSV	12	10	7.2	4.8

Table 8**Catalysts Evaluation****0.9% Pt/USY-1 (Catalyst A)**

[0049] The catalyst was evaluated with Test A. Test results can be found in data table and data plots below.

0.9% Pt/USY-2 (Catalyst B)

[0050] The catalyst was evaluated with Test A and Test B. Test results can be found in data table and data plots below.

0.3% Pt/0.3%Re/Alumina (comparison, Catalyst C)

[0051] This catalyst contained 0.9 wt% Cl and 0.09 wt% S. As discussed above, Catalyst C is a commercially available catalyst.

[0052] The catalyst was evaluated with Test A, Test B (with the first three flow settings) and Test C. Test results can be found in data table and data plots below.

Comparison of Performance of Pt/Re/Alumina and Pt/USY Catalysts

[0053] Table 9 shows test results under Test A conditions. Average data from GC2 to GC6 with stream time from 1.3 hr to 5.3 hr are used. At similar total heptane conversion ranging from 69-73%, Pt/USY catalysts (i.e., Catalysts A and B) provided 27.4-27.5% toluene selectivity vs. 17.6% with 0.3Pt/0.3Re/Alumina. (i.e., Catalyst C).

[0054] Table 10 show test results under Test B conditions (with 0.3Pt/0.3Re/Alumina catalyst (Catalyst C) using the first three flow settings). When compared under the same WHSV and comparable total heptane conversion, Pt/USY-2 catalysts (Catalyst B) provided about 10% higher selectivity for toluene than the 0.3Pt/0.3Re/Alumina catalyst (Catalyst C). For example, at 32 WHSV and 32% total heptane conversion, Pt/USY had 31% toluene selectivity where as 0.3Pt/0.3Re/Alumina had 20%).

Catalyst	0.3Pt/0.3Re/Alumina	0.9Pt/USY-1	0.9Pt/USY-2
Total heptane Conv, %	68.8	70.6	73.2
n-Heptane Conv, %	92.2	93.4	94.2
Toluene Sel, wt%	17.6	27.5	27.4
Toluene Yield, wt%	12.1	19.4	20.1
<u>Yields, wt% (4 hr average)</u>			
Methane	2.58	3.46	3.56
Ethene	0.02	0.00	0.00
Ethane	4.43	3.18	3.26
Propene	0.06	0.02	0.02
Propane	11.76	10.78	11.36
iso-Butane	8.24	4.99	5.53
n-Butane	7.91	8.47	8.62
Butenes, Butadiene	0.14	0.07	0.07
iso-Pentane	6.56	2.55	2.64
n-Pentane	4.00	3.75	3.69
neo-Pentane	0.02	0.01	0.01
Pentenes	0.14	0.06	0.06
Hexanes	7.92	9.13	9.16
Hexenes	0.13	0.12	0.12
Cyclohexane	0.01	0.04	0.04
Methycyclopentane	0.14	0.03	0.14
2,4-Dimethylpentane	0.97	1.38	1.20
2-Methylhexane	7.13	6.66	6.16
3-Methylhexane	8.77	8.23	7.60
n-Heptane	7.71	6.55	5.75
Other Heptanes (2,2-DMP, 2,2,3-TMB, 3,3-DMP, 2,3-MDP, EtP)	6.19	5.91	5.52

Heptens	0.33	0.44	0.40
Methylcycloheptane	0.13	0.22	0.21
Benzene	0.78	2.40	2.58
Toluene	12.10	19.41	20.06
C8+ Hydrocarbon	1.81	2.12	2.23
Sum	100.0	100.0	100.0
Sum of C7 Hydrocarbon	31.24	29.40	26.85
C5+ Hydrocarbon	64.86	69.03	67.59
C1-C6 Hydrocarbon	54.85	49.07	50.86
C7+ Hydrocarbon	45.15	50.93	49.14
Molar Hydrocarbon Ratio			
C1/C6	1.54	1.58	1.59
C2/C5	0.99	1.20	1.22
C3/C4	0.96	1.05	1.05
i-C4/n-C4	1.04	0.59	0.64
C1/C3	0.60	0.88	0.86

Table 9. Comparison of Performance of Pt/Re/Alumina and Pt/USY Catalysts Under Test A Conditions (500°C, 350-360 psig, 10 WHSV, 5:1 H₂/HC, 5.5 hours on stream)

Catalyst	0.3Pt/0.3Re/Alumina			0.9Pt/USY-2				
Hours on Stream	1.3-5.3	7.3-11.3	12.3-13.3	1.3-5.3	7.3-11.3	13.3-17.3	19.3-23.3	25.3
n-Heptane WHSV	50	32	22	50	32	22	16	5
Total heptane	22.3	31.9	40.2	26.0	31.7	39.1	47.1	21
Conv, %								
n-Heptane Conv, %	53.6	65.5	73.5	60.9	68.9	76.6	82.8	53
Toluene Sel, wt%	20.8	20.1	19.2	33.7	31.0	28.7	26.9	32
Toluene Yield, wt%	4.6	6.4	7.7	8.8	9.8	11.2	12.7	7
<u>Yields, wt% (4 hr average)</u>								
Methane	0.81	1.28	1.69	0.94	1.14	1.45	1.82	0.
Ethene	0.02	0.04	0.06	0.01	0.03	0.04	0.06	0.
Ethane	1.55	2.28	2.93	1.14	1.46	1.88	2.33	1.
Propene	0.05	0.10	0.14	0.03	0.07	0.11	0.16	0.
Propane	3.36	4.78	6.06	3.31	4.49	5.99	7.62	2.
iso-Butane	0.93	1.56	2.16	1.03	1.56	2.31	3.18	0.
n-Butane	3.42	4.60	5.61	3.25	4.18	5.27	6.38	2.
Butenes, Butadiene	0.08	0.14	0.21	0.06	0.10	0.16	0.23	0.
iso-Pentane	1.52	2.42	3.23	0.54	0.77	1.09	1.44	0.
n-Pentane	1.93	2.56	3.05	1.88	2.21	2.58	2.91	1.
neo-Pentane	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.
Pentenes	0.08	0.14	0.20	0.05	0.09	0.14	0.19	0.
Hexanes	3.10	4.58	5.75	3.50	4.10	4.91	5.77	2.
Hexenes	0.08	0.14	0.16	0.07	0.11	0.15	0.17	0.
Cyclohexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.
Methycyclopentane	0.02	0.04	0.21	0.00	0.00	0.00	0.00	0.
2,4-Dimethylpentane	0.91	1.12	1.05	1.34	1.57	1.76	1.82	1.
2-Methylhexane	9.89	10.47	10.36	11.42	12.13	12.04	11.22	10
3-Methylhexane	13.72	14.04	13.59	14.82	15.35	15.05	13.94	13
n-Heptane	45.95	34.14	26.21	38.75	30.85	23.19	17.07	46
Other Heptanes (2,2-DMP, 2,2,3-TMB, 3,3-DMP, 2,3-MDP, EtP)	6.43	7.39	7.72	6.62	7.41	7.97	8.05	5.
Heptens	0.70	0.73	0.67	0.83	0.80	0.69	0.64	0.
Methylcycloheptane	0.15	0.15	0.15	0.23	0.23	0.22	0.21	0.
Benzene	0.16	0.29	0.41	0.41	0.47	0.63	0.85	0.

Toluene	4.64	6.41	7.71	8.76	9.82	11.22	12.67	7.
C8+ Hydrocarbon	0.50	0.60	0.66	1.03	1.07	1.16	1.28	0.
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0	10
Sum of C7 Hydrocarbon	77.74	68.05	59.75	74.00	68.34	60.92	52.94	78
C5+ Hydrocarbon	89.77	85.22	81.14	90.24	86.97	82.79	78.23	91
C1-C6 Hydrocarbon	17.12	24.94	31.88	16.21	20.78	26.71	33.11	13
C7+ Hydrocarbon	82.88	75.06	68.12	83.79	79.22	73.29	66.89	86
<u>Molar Hydrocarbon Ratio</u>								
C1/C6	1.30	1.36	1.39	1.26	1.31	1.37	1.44	1.
C2/C5	1.07	1.09	1.10	1.12	1.16	1.21	1.26	1.
C3/C4	1.02	1.02	1.02	1.02	1.03	1.04	1.05	1.
i-C4/n-C4	0.27	0.34	0.39	0.32	0.37	0.44	0.50	0.
C1/C3	0.65	0.72	0.75	0.77	0.69	0.65	0.64	0.

Table 10. Comparison of Performance of Pt/Re/Alumina and Pt/USY-2 Under Test B Conditions (500°C, 350-360 psig, 5:1 H₂/HC)

[0055] Figure 2 plots toluene selectivity vs. total heptane conversion. The data is obtained under Test A, Test B, and Test C conditions. The results again show that Pt/USY catalysts (Catalysts A and B) are more selective for toluene production than that of 0.3Pt/0.3Re/Alumina catalyst (Catalyst C).

Example 3: Catalyst Testing on Naphtha Feed

[0056] A feed with the general properties shown in Table 11, cut to 140-325°F (IBP-FBP), was used for a secondary screening of the Pt-USY catalysts. All testing was performed at 500°C and 350 psig, with H₂:HC ratio of 5:1 (molar). The test duration was 72 hours and the first 24 hours on stream were ignored as a line-out period. Unlike the heptane screening, the feed contained a significant quantity of naphthenes, which makes the reactions significantly endothermic. Although the intention was to run the equipment isothermally, it is noted that some undetected temperature gradients could have formed during screening.

Units			Property	Units
S.G.	SG6060F	0.7403	D86 Dist (9 Pts)	DEGF
Hydrogen	WT%	14.68	IBP	163
Molecular Weight		108.4	5% Off	193
Research Octane	R+0	45.5	10% Off	199
Motor Octane (Clear)	M+0	48.4	30% Off	228
Reid Vapor Pressure	PSI	2.1	50% Off	252
Watson K Factor (Kw)	FACT	12.002	70% Off	280
Total P/O/N/A	WT%		90% Off	316
Total Paraffins		60.3	95% Off	332
Total Olefins		0.0	EP	359
Total Naphthenes		27.0		
Total Aromatics		12.7		

Table 11. Predicted Properties of naphtha feed

[0057] Most of the materials tested with naphtha were Pt supported on USY, although some representatives from each material class were included to ensure the primary screening did not create false negatives. Prior to being placed on oil, the following procedure was used to calcine, reduce, and sulfide discovery samples:

1. Place sample in a sealed tube furnace and flow clean dry air;
2. Ramp temperature from ambient to ~ 120°C at 1°C/min then hold for 2 hrs;
3. Ramp temperature from ~120°C to 450°C at 2°C/min (no hold);
4. Ramp temperature from 450°C to 500°C at 5°C/min then hold for 3 hrs;
5. Switch gas to Nitrogen and purge out air for 30 min;
6. Switch gas to Hydrogen and flow for 6 hrs;
7. Switch gas to 0.2% H₂S in Hydrogen and flow for 6 hrs;
8. Switch gas to Hydrogen and flow for 2 hrs;
9. Cool as fast as possible to $\geq 25^{\circ}\text{C}$ wall temperature;
10. Switch gas to Nitrogen and flow for 2 hrs before removing;
11. Store in Nitrogen purged low humidity box until loading into tubes for testing.

[0058] Samples were then loaded into quartz tubes for testing and transferred into the reactor. The catalysts were brought up to 500°C in a hydrogen environment for 140 minutes prior to the introduction of hydrocarbon.

[0059] Yield-octane curves for several Pt/USY samples are shown in Figure 3 along with the performance of the reference catalysts. The reference catalyst was Catalyst C. One trend observed during primary screening also holds when naphtha is used as a feed: lower aluminum content, and therefore lower acidity of the USY zeolite, prior to further

dealumination improves selectivity. However, in contrast to n-heptane performance, the Pt/USY catalyst's performance approaches that of the PtRe reference (it exceeded the more selective Pt-only performance on heptane feed). This indicates that at least part of the selectivity benefit is reduced when the other major reforming reactions (mostly the facile naphthene dehydrogenation) are included.

[0060] As shown, Pt-USY shows similar gasoline and hydrogen selectivities to the reference catalyst on naphtha feed. Also, Pt-USY appears more stable on naphtha with an order of magnitude lower coke formation. It is therefore possible to take advantage of the lower aging rate by operating at lower hydrogen pressures and higher temperatures to improve gasoline yield without compromising cycle length.

Example 4: Catalyst Testing on Naphtha Feed under Accelerated Aging Conditions

[0061] A feed with properties shown in Table 11, cut to 140-325°F was tested. Testing was performed at 150 psig, H₂:HC ratio of 1.5 (molar), with temperature adjusted to achieve a constant research octane number (RON) of 95. The starting temperature was 485°C for the test. These extreme conditions are designed to completely deactivate the catalysts within one week. Three catalysts were tested for naphtha reforming.

1. 0.3% Pt/0.3%Re/Alumina (Catalyst C)

[0062] The same catalyst used for n-heptane test described in Example 4. This catalyst contained 0.9 wt% Cl and 0.09 wt% S. A 4 cc (2.79 g) of this catalyst was used for naphtha test. Feed flow rate for this catalyst was 1.9 LHSV. Catalyst C is KX-120, which is commercially available.

2. 0.3% Pt/Alumina (Catalyst D)

[0063] This catalyst contained 0.3 wt% Pt, 0.8 wt% Cl and 0.04 wt% S. A 5 cc (3.43 g) of this catalyst was used for naphtha test. Feed flow rate for this catalyst was 1.5 LHSV. Catalyst D is Criterion PHF-45 (0.3wt% Pt on Al₂O₃).

3. 0.9% Pt/USY-1 (Catalyst A)

[0064] This is the same catalyst used for n-heptane test described in Example 3. A 4 cc (1.68 g) of this catalyst was used for naphtha test. Feed flow rate for this catalyst was 1.9 LHSV.

RON	54.8
-----	------

MON	54.0
Total Aromatics	12.6
Naphtha Composition, wt%	
N-Pentane	0.56
Iso-Pentane	0.16
Total C5=	0.00
Cyclopentane	0.18
N-Hexane	6.83
Total C6 I-Para	4.52
Total C6=	0.00
M-Cyclopentane	2.28
Cyclohexane	1.78
Benzene	0.76
N-Heptane	8.00
Total C7 I-Para	7.41
Total C7 N5	3.53
M-Cyclohexane	3.90
Toluene	2.66
N-Octane	6.64
Total C8 I-Para	8.09
Total C8 Naph	7.28
Total C8 Arom	5.35
N-Nonane	4.74
Total C9 I-Para	6.94
Total C9 Naph	5.63
Total C9 Arom	3.36
Total C10 Sats	7.37
Total C10 Arom	0.41
Total C11 Sats	1.05
C11+ Aromatics	0.60
Sum	100.0

Table 12. Naphtha Predicted Feed Properties**Naphtha Test Procedure**

[0065] The catalyst (sized to 14-30 mesh) was loaded to the middle zone of an isothermal, down-flow, fixed-bed, and 3/8" outside diameter stainless steel reactor. After pressure test at 450 psig, the reactor pressure was set at 100 psig and H₂ flow was set at 200 cc/min. The reactor was heated at a ramp rate of 2°C/min from 20°C to 450°C, then at 5°C/min from 450°C to 500°C. After 30 minutes, the reactor was cooled down to 400°C. The reactor pressure was set at 150 psig. Once reaching 150 psig, the H₂ flow rate was reduced to 32 cc/min, and naphtha feed was introduced to the reactor at 7.6 cc/hr. The reactor was heated at a ramp rate of 5°C/min from 400°C to 485°C. Fifteen minutes after the reactor reached 485°C, product analysis was conducted by an on-line GC (60M DB-1, -20°C, 2 min, 8°C/min to 250°C, hold for 30 min). GC analysis was conducted every 2 hour until the end of run. Product RON was calculated from GC

analysis. Reaction temperature was adjusted so that the product RON was maintained at 95. The final temperature of the run was 525°C.

Comparison of Performance of Pt/Re/Alumina, Pt/Re/Alumina, and Pt/USY

Catalysts

[0066] To compare aging rate, temperature required for 95 RON vs. time on stream is plotted in Figure 4. After initial deactivation, the Pt/USY catalyst maintained RON better than the Pt/Re/Alumina, and Pt/USY catalysts, i.e., Pt-USY aged at a lower rate than the Pt/alumina and PtRe/alumina catalysts at temperatures above 500°C.

[0067] To compare hydrogen yield, wt% hydrogen produced at 95 RON vs. time on stream is plotted in Figure 5. The Pt/USY catalyst maintained hydrogen yield better than the Pt/alumina and PtRe/alumina catalysts.

[0068] To further demonstrate lower aging rate of Pt/USY catalyst, the spent catalysts were analyzed for their coke content. The data is shown in Table 13 below. The Pt/USY catalyst had much slower coke formation rate than the Pt/alumina and PtRe/alumina catalysts.

	Pt/USY	Pt/Alumina	Pt/Re/Alumina
Coke on Spent Catalyst, wt%	1.9	11.6	11.2
Days on Stream for Naphtha Run	5.8	3.9	4.6
Coke Formation Rate, wt%/Day	0.3	3.0	2.4

Table 13. Coke Analysis of Spent Catalysts

* * *

[0069] The presently disclosed subject matter is not to be limited in scope by the specific embodiments described herein. Indeed, various modifications of the disclosed subject matter in addition to those described herein will become apparent to those skilled in the art from the foregoing description and the accompanying figures. Such modifications are intended to fall within the scope of the appended claims.

[0070] It is further to be understood that all values are approximate, and are provided for description.

[0071] Patents, patent applications, publications, product descriptions, and protocols are cited throughout this application, the disclosures of each of which is incorporated herein by reference in its entirety for all purposes.

* * *

CLAIMS

1. A process for the preparation of a catalyst suitable for use in a naphtha reforming process comprising:
 - (a) providing a Y zeolite with an initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of at least 150;
 - (b) introducing the Y zeolite to a binder to form an intermediate composition;
 - (c) extruding the intermediate composition;
 - (d) reducing the acidity of the extruded composition to provide a low acid composition; and
 - (e) introducing a noble metal to the low acid composition.
2. The process of claim 1, wherein the initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of the Y zeolite is at least 200.
3. The process of claim 1, wherein the Y zeolite is in an H-form.
4. The process of claim 1, further comprising introducing a polyvinyl alcohol to the Y zeolite prior to extruding the intermediate composition.
5. The process according to any one of claims, wherein the binder includes SiO_2 .
6. The process of claim 5, wherein the intermediate composition has a solid weight ratio of Y zeolite:binder of from about 7:3 to about 9:1 prior to being extruded, based on the total solid weight of the intermediate composition at 1000°F.
7. The process according to any one of claims, wherein reducing the acidity of the extruded composition includes calcining the extruded composition.
8. The process of claim 7, wherein the calcining occurs at a heat up rate of between about 3°F to about 7°F per minute, and the extruded composition is maintained at at least about 1000°F for at least 2 hours.
9. The process of claim 7, wherein reducing the acidity of the extruded composition further includes an ammonium exchange operation.
10. The process of claim 9, wherein the extruded composition at beginning of the ammonium exchange operation has a pH of between about 5.7 to about 5.0 and the

extruded composition at the end of the ammonium exchange operation has a pH of between about 4.5 to about 3.8.

11. The process of claim 9, wherein the ammonium exchange operation includes introducing a NH_4^+ source to a vessel containing the extruded composition, and mixing the NH_4^+ source with the extruded composition.

12. The process of claim 9, wherein reducing the acidity of the extruded composition further includes a steaming operation.

13. The process of claim 12, wherein the steaming operation includes heating the extruded composition to at least 1400°F at a rate of between about 3°F to about 7°F per minute and subsequently introducing steam to the heated composition.

14. The process according to any one of claims, wherein the low acid composition has an alpha acidity of less than 1.0.

15. The process of claim 14, wherein the low acid composition has an alpha acidity of less than 0.5.

16. The process according to any one of claims, wherein the noble metal is selected from platinum, rhenium, and combinations thereof.

17. The process according to any one of claims, wherein the noble metal is added to the low acid composition via a rotating impregnation cone.

18. The process according to any one of claims, further including

(f) drying the composition from (e) to prepare a dried catalyst; and

(g) calcining the dried catalyst.

19. The process according to any one of claims, wherein the catalyst is substantially chlorine free.

20. A process of converting naphtha to a higher-octane hydrocarbon supply comprising:

(a) providing a source of naphtha;

(b) exposing the naphtha to a catalyst to convert the naphtha to a higher-octane hydrocarbon supply, wherein the catalyst is prepared by a process that includes:

- (i) providing a Y zeolite with an initial $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of at least 150;
- (ii) introducing the Y zeolite to a binder to form an intermediate composition;
- (iii) extruding the intermediate composition;
- (iv) reducing the acidity of the extruded composition to provide a low acid composition; and
- (v) introducing a noble metal to the acidity-reduced composition.

21. The process of claim 20, further including blending the higher-octane hydrocarbon supply with a gasoline source.

22. The process of claim 20, wherein the catalyst is substantially chlorine free.

23. A system for converting naphtha to a higher-octane hydrocarbon supply utilizing the process according to any one of claims 20 to 22, the system comprising:

at least one vessel having an inlet to receive at least a portion of the naphtha and an outlet to discharge a stream of converted naphtha, wherein the catalyst is housed in the vessel to convert the naphtha to a higher-octane hydrocarbon supply.

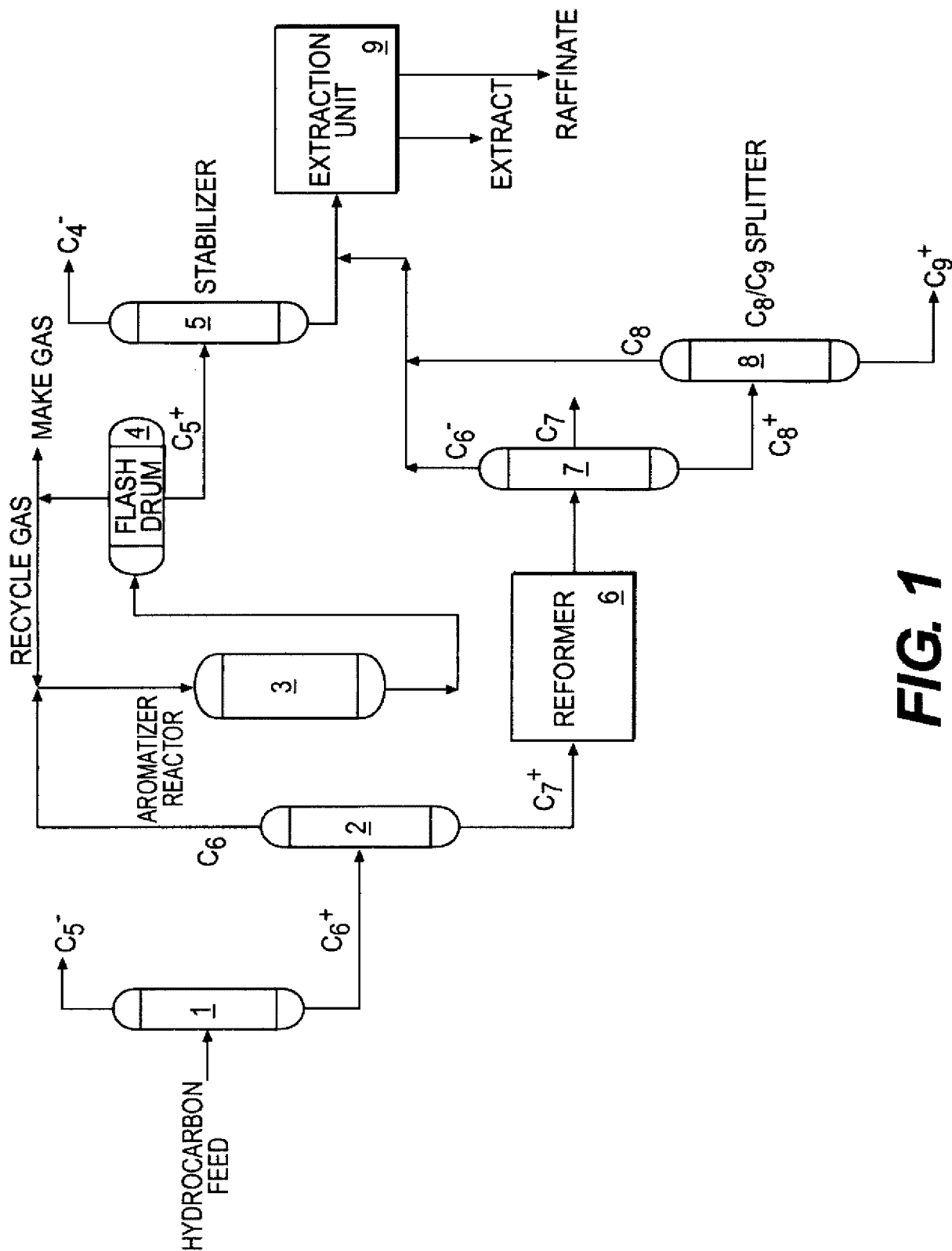


FIG. 1

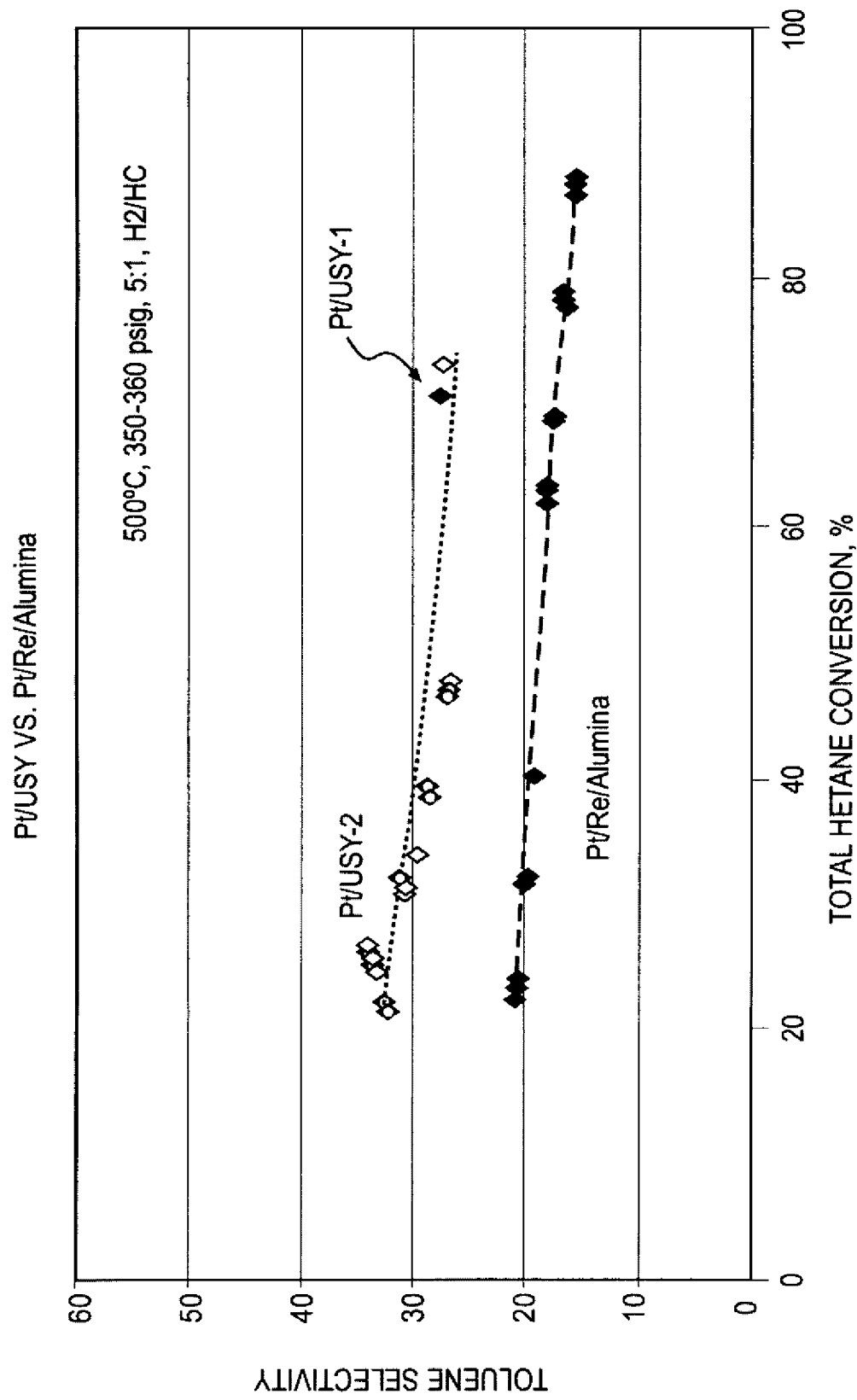


FIG. 2

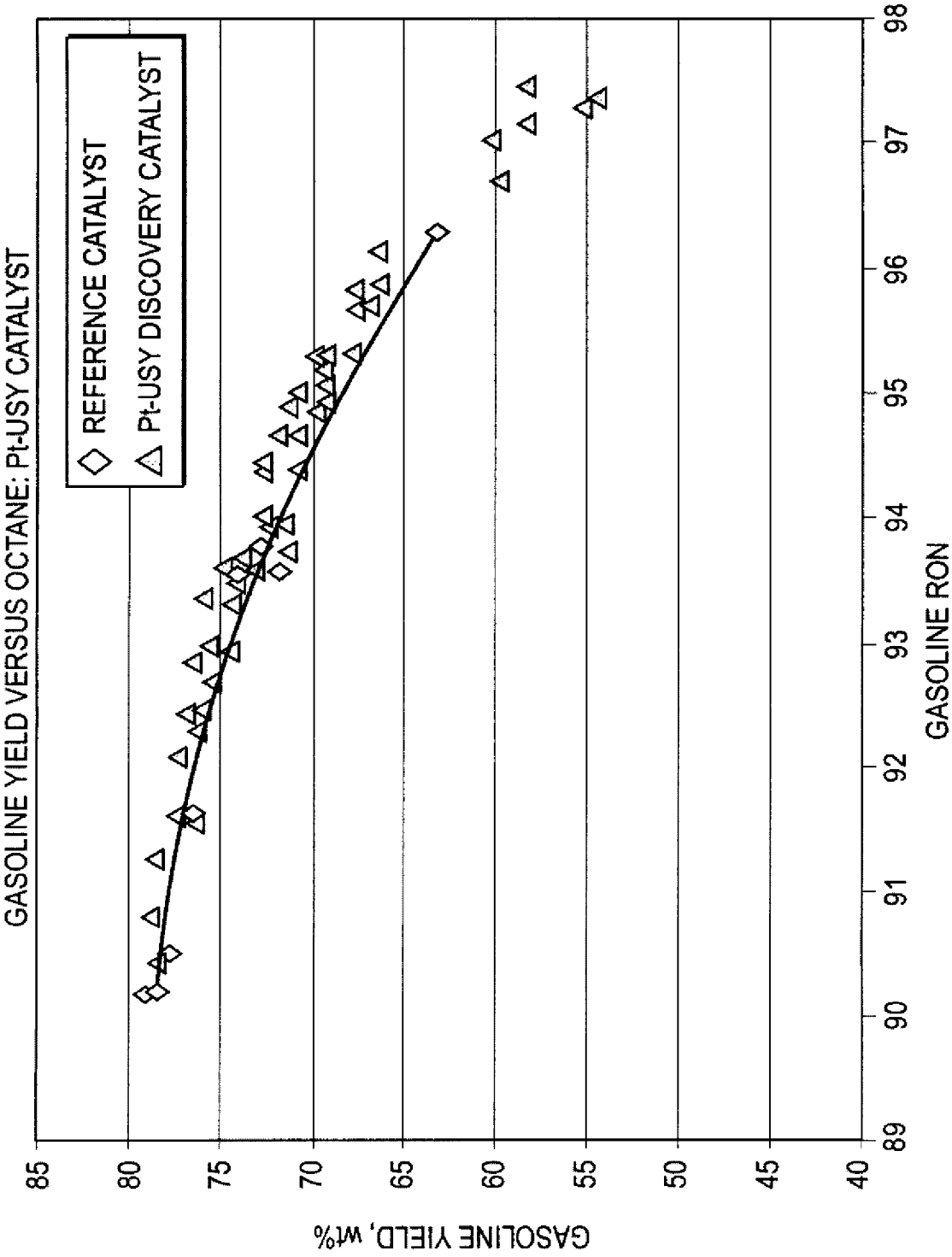
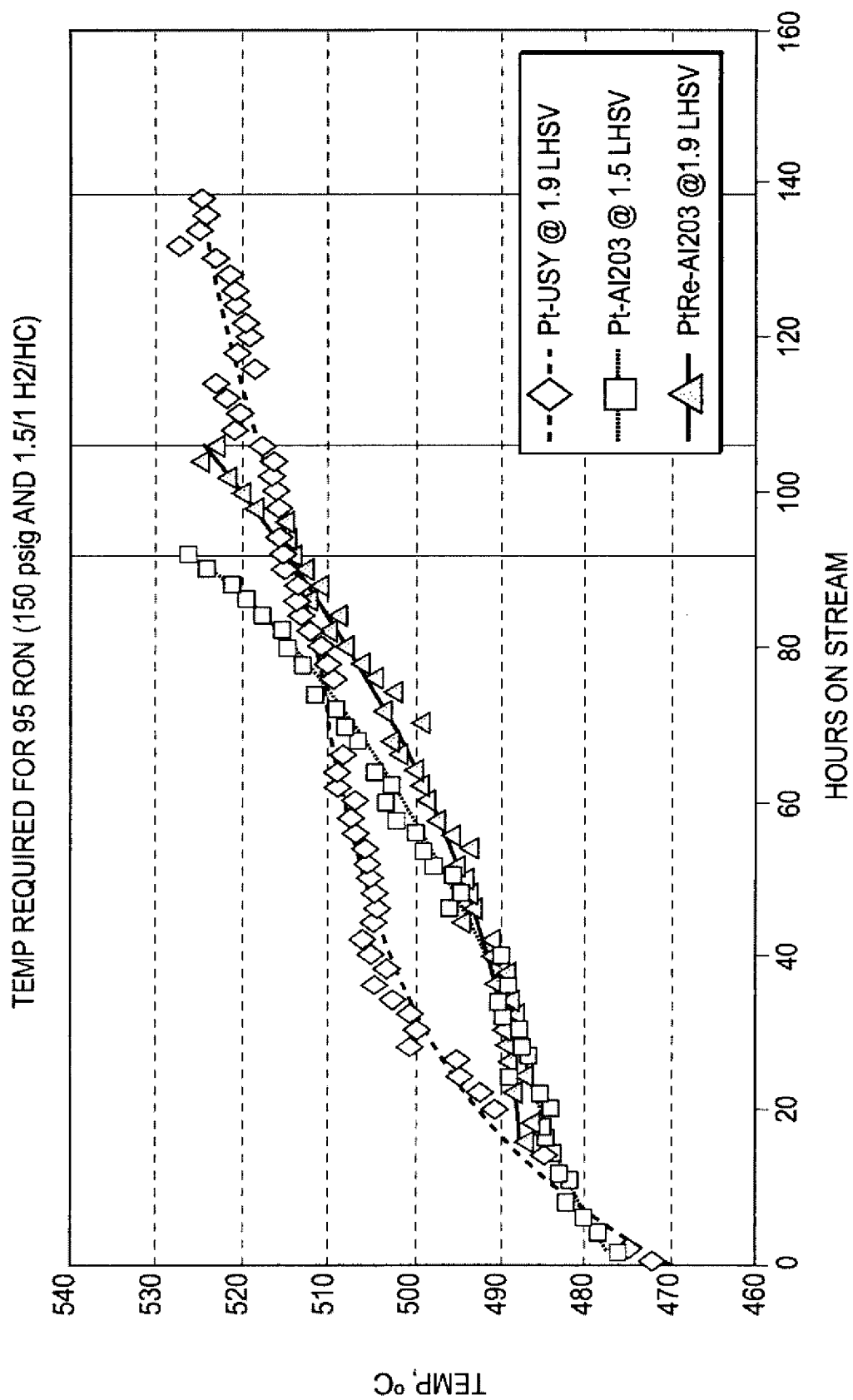
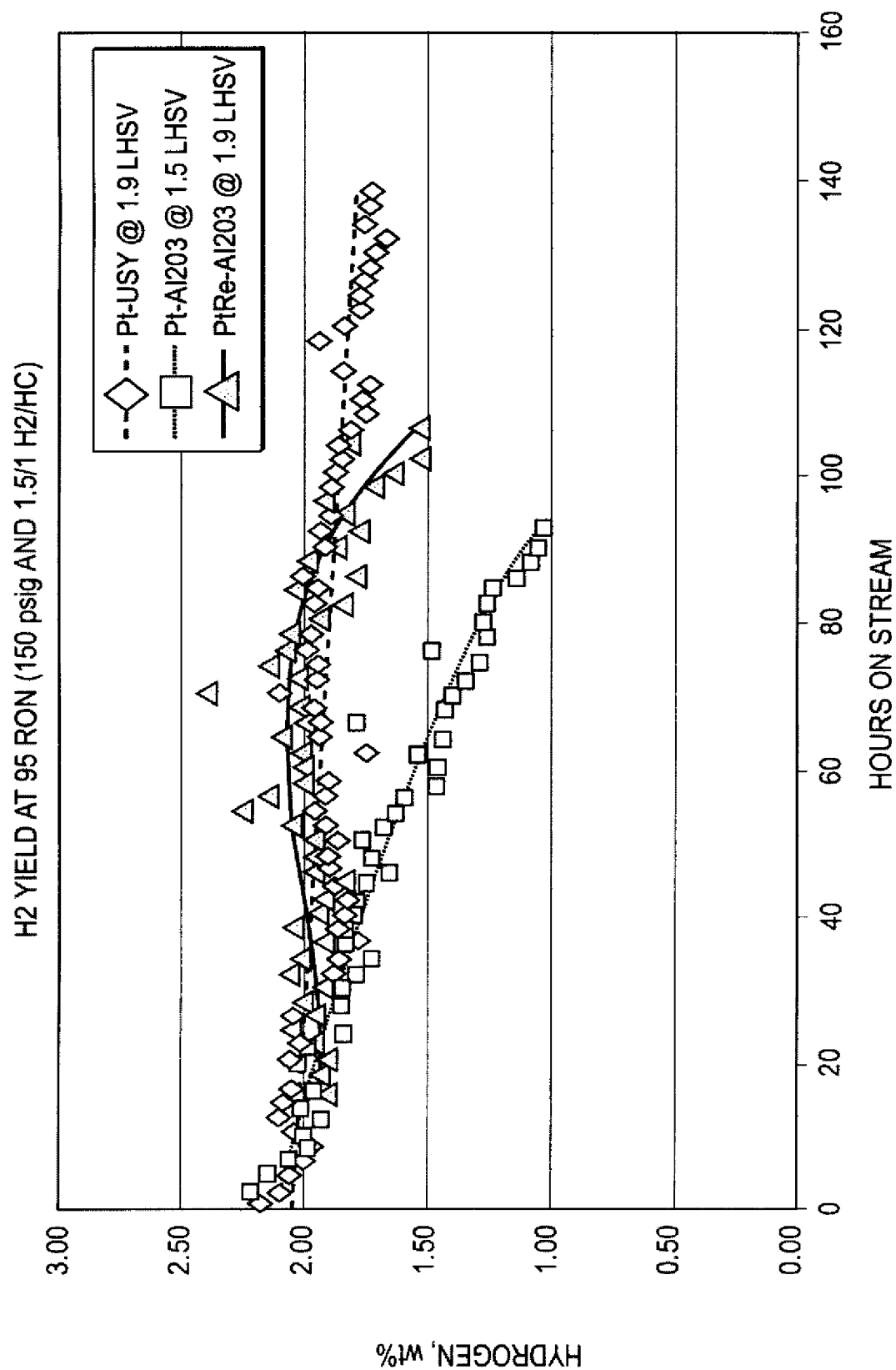


FIG. 3

**FIG. 4**

**FIG. 5**

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/055896

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J29/12 B01J37/10 C07C5/41 C10G35/095
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)

B01J C07C C10G

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 185 484 A (DEL ROSSI KENNETH J [US] ET AL) 9 February 1993 (1993-02-09) claims; example 1 -----	1-23
X	WO 89/04860 A1 (MOBIL OIL CORP [US]) 1 June 1989 (1989-06-01) claims; examples -----	1-23
X	US 4 832 824 A (VAUGHAN DAVID E W [US] ET AL) 23 May 1989 (1989-05-23) claims; examples -----	1-23

☐

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

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14 December 2012

Date of mailing of the international search report

21/12/2012

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/055896

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