BISMUTH- AND PHOSPHORUS-CONTAINING CATALYSTS SUPPORT, REFORMING CATALYSTS MADE FROM SAME, METHOD OF MAKING AND NAPHTHA REFORMING PROCESS

FIELD OF THE INVENTION

This invention relates to bismuth and phosphorus-containing catalyst supports, naphtha reforming catalysts made from such supports, methods of making both support and catalyst, and to a naphtha reforming process using such catalysts.

BACKGROUND OF THE INVENTION

Catalytic naphtha reforming is an important oil refining process that converts low-octane paraffins- and naphthenes-rich naphtha to high-octane, aromatics-rich C_5+ liquid reformate and hydrogen (H_2). Petroleum refiners are always searching for improved reforming catalysts that afford high selectivity (i.e., high C_5+ liquid and H_2 yields), high activity, low coking rates and high selectivity and/or activity stability. More selective catalysts are desired to maximize the production of valuable C_5+ liquid and H_2 while minimizing the yield of less desirable C_1 - C_4 gaseous products. Catalysts with acceptable selectivity but higher activity are also desired because they allow operation at lower reactor inlet temperatures while maintaining the same conversion (octane) level or allow operation at the same temperature but at higher conversion (octane) level. In the former case, the higher activity of the catalysts also allows for significant extension of the cycle length and reduced frequency of regeneration. Catalysts that afford lower coke make rates and higher selectivity and/or activity stability are also very highly desired because they allow for significant shortening of the coke burn off and unit turnaround time or for a longer operation before regeneration.

Many researchers have devoted their efforts to the discovery and development of improved reforming catalysts. The original commercial catalysts employed a platinum-group metal, preferably platinum itself, deposited on a halogen-acidified γ-alumina support; see, for example, Haensel's U.S. Pat. Nos. 2,479,109-110, granted in 1949 and assigned to Universal Oil Products Company. About 1968, the use of rhenium together with platinum was introduced. Kluksdhal's U.S. Pat. No. 3,415,737 teaches Pt/Re catalysts wherein the atomic ratio of rhenium to platinum is between 0.2 and 2.0 and his U.S. Pat No. 3,558,477 teaches the importance of holding the atomic ratio of rhenium to platinum to less than 1.0. Buss's U.S. Pat. No. 3,578,583 teaches the inclusion of a

minor amount, up to 0.1 percent, of iridium in a catalyst having up to 0.3 percent each of rhenium and platinum. Gallagher *et al.'s.* U.S. Pat. No. 4,356,081 teaches a bimetallic reforming catalyst wherein the atom ratio of rhenium to platinum is between 2 and 5.

Phosphorus has been known to increase aromatics yield when included in reforming catalysts since at least 1959 when Haensel taught the same in U.S. Pat. No. 2,890,167. In U.S. Pat. No. 3,706,815, Alley taught that chelating ions of a Group VIII noble metal with polyphosphoric acid in a catalyst enhanced isomerization activity. And Antos *et al.'s* U.S. Pat. Nos. 4,367,137, 4,416,804, 4,426,279, and 4,463,104 taught that the addition of phosphorus to a noble-metal reforming catalyst results in improved C_5+ yields.

In 1974-5, Wilhelm's U.S. Pat. Nos. 3,798,155, 3,888,763, 3,859,201 and 3,900,387 taught the inclusion of bismuth in a platinum-group reforming catalyst to improve selectivity, activity and stability characteristics. Antos' U.S. Pat. No. 4,036,743 taught a hydrocarbon conversion catalyst comprising platinum, bismuth, nickel and halogen components. More recently, Wu *et al.'s* U.S. Pat Nos. 6,083,867 and 6,172,273 Bl teach a reforming catalyst of mixed composition or stage-loaded comprising a first catalyst comprising platinum and rhenium on a porous carrier material and a second catalyst comprising a bismuth and silica component

Until now, however, no one has taught the benefits of including both bismuth and phosphorus in a noble-metal naphtha reforming catalyst.

SUMMARY OF THE INVENTION

This invention provides for a catalyst support comprising γ-alumina and a concentration of bismuth between 0.05 wt. % and 0.1 wt. % and a concentration of phosphorus between 0.05 wt. % and 0.6 wt. % incorporated homogeneously throughout. The invention further provides for catalyst compositions comprising amounts of platinum between 0.1 wt. % and 1 wt. % of the catalyst and amounts of chlorine between 0.05 wt. % and 2 wt. % of the catalyst and optionally rhenium in an amount between 0.01 wt. % and 1 wt. % deposited on such supports. The invention also provides for a method of making such catalyst support and catalyst compositions and for a process for reforming naphtha to improve its octane using such catalyst. When used to catalyze reforming naphtha, the Bi- and P-containing catalyst compositions of this invention unexpectedly exhibited significantly lower coking rates and C_5+ yields and activity decline rates; i.e., higher stability, relative to catalysts containing only either Bi or P previously known.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows C_5+ Yield Decline Data for Catalysts A to H.

Figure 2 shows Activity Decline Data for Catalysts A to H.

Figure 3 shows C_5+ Yield Decline Data for steamed and oxychlorinated Catalysts D_{so} and G_{so}.

Figure 4 shows Activity Decline Data for steamed and oxychlorinated Catalysts D_{so} and G_{so}.

Figure 5 shows C_5+ Yield Decline Data for Catalysts I to L.

Figure 6 shows Activity Decline Data for Catalysts I to L.

DETAILED DESCRIPTION

The catalyst support compositions of the present invention comprise alumina, primarily γ-alumina, into which amounts of bismuth between 0.05 wt. % and 0.1 wt. % and amounts of phophorous between 0.05 wt. % and 0.6 wt. % have been incorporated during preparation of the support extrusion mixture. It has been found that, for catalysts made from such supports, the inclusion of these amounts of both Bi and P distributed essentially homogeneously throughout the support results in significant improvement in the C_5+ yield and activity stability relative to the conventional catalyst compositions. In addition, these promoters in the support allow for significant suppression of the coking rate and remarkable improvement in the regenerability of the catalyst after moisture upset.

The catalyst compositions of this invention comprise such support impregnated with amounts of platinum between 0.1 wt. % and 1 wt. % of the catalyst and amounts of chlorine between 0.05 wt. % and 2 wt. % of the catalyst and optionally an amount of rhenium between 0.01 wt. % and 1 wt. %. The amount of Pt in the catalyst provides the desired hydrogenation-dehydrogenation functionality of the catalyst, the amount of Re (when present) improves the coke tolerance and resistance to deactivation, and the amount of Cl enhances the acidity of the support and provides the desired acidic (isomerization and cracking) functionality. Inclusion of Pt, Re and Cl in a naphtha reforming catalyst is well known in the art. However, when these elements are impregnated onto the supports of the present invention, these catalysts exhibit significantly lower coking rates and higher C_5+ yield and activity stability than catalysts comprising the same elements impregnated onto conventional supports. The catalyst compositions of the present invention, therefore, allow for a reduction of the frequency of catalyst regeneration and maximization of unit

uptime, reformate production and profitability. In the rare cases when higher stability is not desired, these compositions would still provide significant cost savings to the refiner because of their lower coke make rates, shorter coke burn off time and unit turnaround time during regeneration relative to conventional catalysts. The lower coking rates of the compositions of this invention could be of a great benefit to refiners operating the two different types of fixed-bed reforming units: cyclic and semi-regenerative.

Support

The support for the catalyst of the present invention comprises an alumina that is predominately γ-alumina throughout which a concentration of bismuth between 0.05 wt. % and 0.1 wt. % and a concentration of phosphorus between 0.05 wt. % and 0.6 wt. % have been essentially homogeneously distributed.

These amounts of bismuth and phosphorus are distributed throughout the support particles by incorporation of these promoters into the support precursor mixture prior to forming the support particles, which is usually accomplished by extrusion. Between 0.05 wt. % and 0.08 wt. %, based on the finished catalyst, of bismuth has been found to be preferred. Between 0.1 wt. % and 0.4 wt. %, based on the finished catalyst, of phosphorus is preferred, with between 0.25 wt. % and 0.35 wt. % being particularly preferred.

The forming of the support particles may be accomplished by any of the methods known to those skilled in the art. In the preferred method, a mixture comprising approximately 62 wt. % of γ-alumina powder and 38 % wt. alumina sol is prepared. The γ-alumina is a high-purity γ-alumina made by digestion of aluminum wire in acetic acid followed by aging to form alumina sol and spray drying of the sol to form the alumina powder. The alumina sol is also prepared as described above (i.e., by digesting aluminum wire in acetic acid and aging) and contains about 10 wt. % alumina (dry basis), 3 wt. % of acetic acid and the remainder deionized water. The alumina sol is blended with the alumina powder and acts as a peptizing agent to aid the extrusion of the γ-alumina. Any other methods (other than using alumina sol; for example, using extrusion aids) known to those skilled in the art could also be used to form the alumina carrier particles of this invention. Such extrusion aids include but are not limited to acids (such as nitric, acetic, citric, etc.) and/or organic extrusions aids (such as methocel, PVI, steric alcohols, etc.)

The desired amounts of phosphorus and bismuth are essentially homogeneously incorporated into the finished support by adding to the γ-alumina/alumina sol mixture

being blended an amount of phosphorus precursor solution sufficient to provide the desired concentration of phosphorus on the finished support and then an amount of the bismuth precursor solution sufficient to provide the desired concentration of bismuth on the finished support. The addition of phosphorus and bismuth solutions is accomplished at a slow rate followed by a period of continued blending to ensure homogeneous distribution of phosphorus and bismuth in the support. The final mix should be prepared in such a way so that to form an extrudable paste. Well extrudable paste is formed when the LOI (loss on ignition) of the mixture is between 30 and 70 wt. %, and more preferably between 45-60 wt. %.

To incorporate the desired amount of phosphorus into the support a solution of phosphorus precursor is prepared. The solution can be prepared by any of the methods known to those skilled in the art. The phosphorus precursor is selected from the group comprising phosphorus-containing acids and salts, for example, H_3PO_4, H_3PO_3, H_3PO_2, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, with H_3PO_4 being the most preferred precursor. The preferred precursor solution may contain between 50 and 85 wt. % H_3PO_4, with 70-85 wt. % H_3PO_4 being the most preferred.

To incorporate bismuth into the support in such a way so as to provide for a homogeneous distribution of the bismuth atoms, it is essential that a bismuth solution having all bismuth cations completely in solution and not indirectly interacting with each other (via chemical bonds with other elements) be used. A number of bismuth precursors, including but not limited to $Bi(NO_3)_3$ $5H_2O$, $BiCl_3$, BiOCl, $BiBr_3$, Bi acetate, Bi citrate, and various Bi alcoxides may be used, with $Bi(NO_3)_3$ $5H_2O$ being the most preferred. Solutions of these precursors in water, water + complexing agents (to improve Bi solubility), acidified water solutions as well as different surfactants or organic solvent solutions may all be used to prepare the Bi-containing supports and catalysts of the present invention. The acceptable concentration of bismuth in the solution is dependent on the bismuth precursor chosen, the nature of the solvent and the solubility range for the precursor in the solvent. The most preferred bismuth solution contains about 9 wt. % Bi (from $Bi(NO_3)_3$ $5H_2O$) and approximately 10 wt. % d-mannitol (a complexing agent) and the balance water. Other complexing or chelating agents , including but not limited to polyacohols or mixtures of polyacohols or alcohols and acids could also be used instead of d-mannitol to achieve complete dissolution of the bismuth precursor in the solvent.

The same effect could also be achieved by using acidified water solutions of the bismuth precursor.

The final steps in making the support of the present invention are forming the paste prepared above into particles of the support, followed by drying and, optionally, calcining. Any of the conventional support shapes, such as spheres, extruded cylinders and trilobes, etc. may be employed. The formed particles may be dried by any of the methods known to those skilled in the art. However, drying at low temperature, that is between 110° C and 140° C for over 10 hours is preferred. Drying should achieve a final support LOI level in the range of 10 wt. % to 36 wt. %, more preferably 17 wt. % to 36 wt. %. It is preferred that the dried support particles then be calcined in order to lower their LOI to between 1 wt. % and 10 wt. %, preferably between 1 wt. % and 7 wt. %. Calcination is done at a temperature between 400° C and 750° C, preferably between 550° C and 700° C for a period of between 30 minutes and 5 hours, preferably between 1 hour and 2 hours.

The finished supports of the present invention are all characterized by having an essentially homogeneous distribution of bismuth and phosphorus throughout the γ-alumina base material.

Catalysts

To form the finished catalysts of this invention, amounts of platinum between 0.1 wt. % and 1 wt. % of the catalyst and amounts of chlorine between 0.05 wt. % and 2 wt. % of the catalyst and optionally amounts of rhenium between 0.05 wt. % and 0.6 wt. % are deposited on the support by impregnation techniques known to those skilled in the art. Between 0.15 wt. % and 0.6 wt. %, based on the finished catalyst, of platinum has been found to be preferred, with between 0.20 wt. % and 0.30 wt. % being particularly preferred. Between 0.8 wt. % and 1.2 wt. %, based on the finished catalyst, of chlorine has been found to be preferred, with between 0.9 wt. % and 1.1 wt. % being particularly preferred. If rhenium is present, between 0.1 wt. % and 0.5 wt. %, based on the finished catalyst, of rhenium has been found to be preferred, with between 0.2 wt. % and 0.45. wt. % being particularly preferred.

Various Pt, Cl and Re precursors known to those skilled in the art can be used to prepare impregnating solutions and to impregnate the support of this invention. Such

precursors include but are not limited to chloroplatinic acid, bromoplatininc acid, ammoniumchloroplatinate, tetrachloroplatinate, dinitrodiaminoplatinum, hydrochloric acid, tetrachloromethane, chloromethane, dichloromethane, 1,1,1-trichloroethane, ammonium chloride, perrhenic acid, and ammonium perrhenate. Any precursor that will decompose in water, thereby providing the necessary ions for deposition on the support, is acceptable. In addition, the impregnating solution may contain small amounts of different acids such as nitric, carbonic, sulfuric, citric, formic, oxalic, etc. which are known to those skilled in the art to improve the distribution of the platinate and, in the case of rhenium, the perrhenate anions on the alumina carrier. The Pt, Cl and optionally Re concentration of the impregnating solution is determined in such a way to achieve the desired concentration of these components on the finished catalyst. All impregnation techniques known to those skilled in the art may be used to prepare the catalysts of this invention.

Process for Reforming Naphtha

Reforming of hydrotreated naphtha feed may be achieved by contacting such feed with the catalyst of the present invention in the presence of hydrogen at elevated temperature and pressure. The operating conditions are a space velocity between 0.5 hr^{-1} and 6 hr^{-1}, preferably between 1 hr^{-1} and 3 hr^{-1}, a pressure of between about 0.1 MPa and about 3.5 MPa, preferably between 1 MPa and 3 MPa, a temperature between about 315° C and about 550° C, preferably between 480° C and 540° C, a hydrogen recycle gas to hydrocarbon feed ratio between about 1 mol/mol and 10 mol/mol, preferably between about 1.5 mol/mol and 8 mol/mol, and more preferably between about 2 mol/mol and 6 mol/mol.

EXAMPLES

The following examples illustrate the preparation of the supports and catalysts of this invention. A number of examples illustrate the use of such catalysts in reforming of naphtha and compare their performance to conventional naphtha reforming catalysts. These examples should not be considered as limiting the scope of this invention.

EXAMPLE 1

This example describes the preparation of five catalyst supports, catalyst supports B, C and D are of the present invention each containing a different concentration of bismuth..

Support A was prepared by mixing 1 kg of γ-alumina with 627 g of alumina sol in a blender for 10 minutes. With the blender running, 9.1 g of 85 wt. % H_3PO_4 were slowly added and blending continued for about another minute. Then, the bismuth solution defined in Table 1 for Support A was added to the blender and the blending was continued for another 7 minutes to form an extrudable paste. The paste was extruded into 1.6 mm diameter pellets which were dried at 125° C overnight. The pellets were then sized to a predominant length of 4 to 6 mm and calcined at 660° C for 1.5 hours. The finished Support A had the composition shown in Table 1.

Supports B, C, D and E were prepared in the same manner, except that Solution A was replaced with the solution appropriate for each support as shown in Table 1.

Table 1

Support	A	B	C	D	E
Solution:					
g$Bi(NO_3)_3$-$5H_2O$	3.20	1.87	1.49	1.12	0.747
g d-mannitol	1.50	0.90	0.72	0.54	0.36
g deionized H2O	10.0	6.0	4.5	3.5	2.5
Finished Support:					
Bi, wt.%	0.17	0.10	0.08	0.06	0.04
P, Wt.%	0.3	0.3	0.3	0.3	0.3
Al_2O_3	Balance	Balance	Balance	Balance	Balance

A small sample of Support D was sulflided by mounting a few pellets on the bottom of a glass Petrie dish, adding a drop of 20 wt. % ammonium sulfide solution, closing the glass lid, and allowing the pellets to be exposed to the ammonium sulfide vapors for about 10 minutes. During this treatment the bismuth atoms in the extrudate reacted with the ammonium sulfide, yielding dark gray bismuth sulfide. Examination of the sulfided pellets showed them to be uniformly dark gray, in contrast to the milky-white un-sulfided pellets, confirming that the bismuth atoms were homogeneously distributed throughout the support.

EXAMPLE 2

(Comparative)

This example describes the preparation of three conventional catalyst supports, Support F comprising alumina containing the same concentration of bismuth as Support D of Example 1, i.e., 0.06 wt. %; Support G comprising alumina containing the same concentration of phosphorus as the supports of Example 1, i.e., 0.3 wt. %; and Support H comprising pure alumina.

Support F was prepared following the procedure described in Example 1 except no H_3PO_4 was added. Support G was prepared following the procedure described in Example 1 except no Bi/d-mannitol solution was added. Support H was prepared in like manner except neither H_3PO_4 nor Bi/d-mannitol solution was added.

EXAMPLE 3

This example describes the preparation of five catalysts catalysts B, C and D are of the present invention each containing a different concentration of bismuth in its support.

Five impregnating solutions were prepared, each by mixing 0.77 ml of concentrated HNO_3, 1.97 ml of concentrated (12M) HCl and 0.660 g of a solution of chloroplatinic acid (denoted as CPA, 29.7 wt. % Pt) and 30 ml of deionized water. The solutions were stirred and another 120 ml of deionized water were added to bring the total volume of each of the impregnating solutions to 150 ml. The solutions were then placed in a 500 ml. graduated cylinder and circulated with the aid of a peristaltic pump. In addition, CO_2 gas was bubbled at a very low rate through a gas dispersion tube placed in the bottom of the graduated cylinder and into the solution. This was done in order to provide HCO_3 anions which are known to those skilled in the art as capable of competing with Pt and Re anions for alumina surface and to provide for better distribution of these metals on the alumina support.

To impregnate each of Supports A-E from Example 1, once the solution circulation and CO_2 gas bubbling were established, 70 g of the support were quickly added to the solution in the cylinder. The impregnating solution was then circulated over the support for 3 hrs while bubbling CO_2 and then the CO_2 gas and the circulation were stopped. The solution was drained and the catalyst was dried at 125° C for 2 hr and at 250° C for 4 hrs and then calcined at 525° C for 1.5 hrs. Each of the finished catalysts, designated Catalysts A-E corresponding to Supports A-E, were analyzed and found to

contain about 0.25 wt.% Pt, about 0.95 wt.% Cl and the corresponding amounts of Bi and P (See Example 1, Table 1).

EXAMPLE 4
(Comparative)

This example describes the preparation of three conventional catalysts.

Three more impregnating solutions were prepared. These solutions were identical to those prepared in Example 3 except that 0.754 g of CPA solution were used instead of the 0.660 g of Example 3. Conventional Supports F, G and H from Example 2 were impregnated with these solutions in the same manner as in Example 3. Analysis of the finished catalysts showed Catalyst F to contain about 0.3 wt.% Pt and 1.0 wt. % Cl on a support containing 0.6 wt.% Bi, Catalyst G to contain about 0.30 wt.% Pt and 1.0 wt. % Cl on a support containing 0.3 wt.% P, and Catalyst H to contain about 0.30 wt.% Pt and 0.96 wt. % Cl on a support containing neither Bi nor P.

EXAMPLE 5

This example describes the steaming and regeneration via oxychlorination treatments of Catalyst D from Example 3 and Catalyst G from Example 4.

Steaming: 40 g quantities of Catalysts D and G were placed in stainless steel racks and into a programmable furnace equipped with inlet and outlet lines. The furnace was closed and an airflow was established through the lines and the furnace chamber. The furnace temperature was then ramped from ambient to 500° C while maintaining the airflow. Once 500° C temperature was reached the airflow was turned off and a slow flow of water was established through the inlet line and into the heated furnace chamber. The water evaporated in the furnace chamber and steam was generated. The catalyst samples were subjected to steaming in the furnace for 16 hrs to insure significant Pt agglomeration. Then, the water was stopped, the heat was turned off and the airflow was again established. The samples were then cooled to 150° C and transferred to an airtight container. Although there was evidence of Pt agglomeration on both samples, the steamed Catalyst D was much lighter in color than the steamed Catalyst G (which was darker gray), indicating higher resistance for Pt agglomeration for the Bi- and P-containing Catalyst D of this invention.

Oxychlorination: Following the steaming treatment, both catalyst samples were subjected to a two-stage oxychlorination treatment. Such treatments are known to be able to restore the original high dispersion of the Pt on an alumina support and are extensively practiced by those skilled in the art to restore Pt dispersion, activity and selectivity of spent Pt reforming catalysts. In the first stage, a 2% mol O_2/N_2 plus Cl_2 gas carrying H_2O and HCl vapors was passed through the catalyst bed at 500° C for 5.5 hrs. In the second stage, the Cl_2 gas was turned off and 2% mol O_2/N_2 gas carrying H_2O and HCl vapors was passed through the catalyst bed for another 5.5 hrs. The purpose of the first stage was to redisperse the Pt on the support to a level similar to that of the fresh catalyst, whereas the purpose of the second stage was to adjust the Cl to the desired level. The steamed and oxychlorinated sample of Catalyst D was designated Catalyst D_{SO} and the similarly treated sample of Catalyst G was designated Catalyst G_{SO}. A visual inspection of Catalyst D_{SO} revealed the absence of grayish colored pellets, indicating no agglomerated Pt. In contrast, the inspection of Catalyst G_{SO} revealed the presence of grayish colored pellets. This indicates that the Bi- and P- containing Catalyst D of this invention better preserves and restores its Pt dispersion upon steaming and oxychlorination treatments than the conventional Catalyst G which contained phosphorus but no bismuth. Both catalysts were analyzed and found to contain very similar levels of Cl (0.83 wt.% and 0.81 wt.%, respectively).

EXAMPLE 6

This example describes the preparation of a Pt- and Re-containing catalyst of this invention.

An impregnating solution was prepared from 0.50 ml of concentrated HNO_3, 1.89 ml of concentrated (12M) HCl and 0.660 g of a solution of CPA (29.7%w Pt), 0.302 g of NH_4ReO_4 and 50 ml of deionized water. The solution was stirred and more deionized water was added to bring the total volume of the solution to 150 ml. The solution was then placed in a 500 ml graduated cylinder and circulated with the aid of a peristaltic pump. In addition, CO_2 gas was bubbled at a very low rate through a gas dispersion tube placed in the bottom of the graduated cylinder and into the solution. Once the solution circulation and CO_2 gas bubbling were established, 70 g of Support D from Example 1 was added to the impregnating solution. The impregnating solution was circulated over the support for a period of 3 hrs while bubbling CO_2 gas and then the CO_2 and the

circulation were stopped. The solution was drained and the catalyst was dried at 125° C for 2 hr and at 250° C for 4 hrs and calcined at 525° C for 1.5 hrs. The finished catalyst was designated Catalyst I and on analysis was found to contain about 0.25 wt.% Pt, 0.26 wt.% Re, 0.99 wt.% Cl, 0.06 wt.% Bi, 0.30 wt.% P and the remainder alumina.

EXAMPLE 7
(Comparative)

This example describes the preparation of samples of Pt- and Re-containing catalysts on conventional supports F, G and H of Example 2.

Samples of Supports F, G and H were each impregnated using the impregnating solution and procedure described in Example 6. The finished catalyst made from Support F, designated Catalyst J, was analyzed and found to contain 0.26 wt.% Pt, 0.24 wt.% Re, 0.06 wt.% Bi and 0.95 wt.% Cl. The finished catalyst made from Support G, designated Catalyst K, was analyzed and found to contain 0.25 wt.% Pt, 0.25 wt.% Re, 0.3 wt.% P and 0.98 wt.% Cl. The finished catalyst made from Support H, designated Catalyst L, was analyzed and found to contain 0.25 wt.% Pt, 0.25 wt.% Re and 0.96 wt.% Cl.

The following examples measure and compare the performance of the catalysts prepared above. In measuring catalyst performance in the reforming of naphtha, four terms are employed - selectivity, activity, stability and coking rate:

"Selectivity" is a measure of the yield of C_5+ liquids, expressed as a percentage of the volume of fresh liquid feed charged.

"Activity" is a measure of the reactor temperature required to achieve the target product octane.

"Stability" is a measure of a catalyst's ability to sustain its selectivity and activity over time. It is expressed as and is inversely proportional to the selectivity and activity decline rates.

"Coking Rate" is a measure of the tendency of a catalyst to make coke on its surface during the reforming process. Because reforming catalysts deactivate by a mechanism of coke deposition, catalysts with lower coking rates usually exhibit lower C_5+ yield and Activity decline rates; i.e., higher stability than catalysts with higher coking rates.

EXAMPLE 8

This example compares the performance of Catalysts A to H when used to reform a full range (C_5-C_{12} hydrocarbons) commercial hydrotreated naphtha feed having a paraffins/naphthenes/ aromatics (P/N/A) content of 51/34/15 wt.%, respectively.

All tests were done in stainless steel micro-reactors operating under pseudo-adiabatic and once-through H_2 regime and equipped with feed and product tanks and an online full product (H_2 + C_1-C_{12} hydrocarbons) gas chromatograph analyzer. The catalysts were loaded in the micro-reactors as whole particles (not crushed). In each test, 38 cc of catalyst and 38 cc of SiC (an inert diluent) were loaded in the micro-reactor in four stages as shown in Table 2.

Table 2

Stage	Catalyst, cc.	SiC, cc
1 (inlet)	1.9	17.1
2	5.7	13.3
3	11.4	7.6
4 (outlet)	19.0	0

The feed was doped with isopropanol and 1,1,1-thrichloroethane to provide the desired target levels of 20 ppmv of H_2O and 1 ppmv of Cl in the gas phase. The "extra" (unwanted) water in the feed was removed prior to the test by passing the feed trough a vessel filled with 4A molecular sieve. The tests were conducted as constant-octane (99 C_5+ RON) deactivation (Stability) tests at 2.4 hr^{-1} LHSV, 1.03 MPa and 3 mol H_2/mol HC. These conditions, as well as the above catalyst loading arrangement were chosen in order to force the catalyst to perform harder and decline faster. In order to maintain the product octane (C5+RON) at constant level throughout the run the reactor wall temperature was adjusted as needed to correct for the Activity decline.

Figures 1 and 2 show the C_5+ yield decline and Reactor Wall Temperature (Activity decline) data, respectively, for Catalysts A to H. Table 3 shows the corresponding Activity and C_5+ yield decline rates and Coking rates. The analysis of the data reveals that the Bi-containing Catalyst F exhibited the lowest Coking Rate and C_5+ yield and Activity decline (i.e., the highest Stability) among the conventional catalysts. Also, comparison of the data for Catalysts G and H reveals that the addition of P to the

carrier provides somewhat better C_5+ yields but decline and Coking rates similar to the pure alumina-supported Catalyst H. Therefore, the addition of P alone does not suppress the Coking Rate and does not improve the Stability of reforming catalysts. In contrast, comparison of the decline data for the Bi- and P-containing catalysts of this invention shows that their Coking rates and decline rates depend very strongly on the Bi concentration. Surprisingly, Catalysts B, C and D, containing 0.10 wt.% to 0.06 wt.% Bi and 0.3 wt.% P exhibited significantly lower Coking rates and C_5+ yield and Activity decline rates; i.e., higher Stability relative to the catalysts made from supports containing Bi-only, P-only, and pure alumina, Catalyst F, G and H. These data demonstrate that the inclusion of the proper concentrations of both Bi and P in a carrier used to make naphtha reforming catalysts has a synergistically beneficial effect on Coking Rate and performance.

Table 3

Catalyst	Pt/Bi/P, wt.%	Ave. Hourly Decline Rates: Activity, °C/hr.	C_5+ Yield, vol.%/hr.	Coking Rate, wt.%/hr.
A	0.25/0.17/0.3	+0.357	-0.069	+0.074
B	0.25/0.1/0.32	+0.270	-0.043	+0.058
C	0.25/0.07/0.28	+0.270	-0.034	+0.054
D	0.26/0.06/0.29	+0.258	-0.045	+0.052
E	0.26/0.04/0.3	+0.332	-0.056	+0.068
F	0.24/0.06/0	+0.300	-0.054	+0.061
G	0.3/0/0.3	+0.458	-0.087	+0.072
H	0.3/0/0	+0.390	-0.095	+0.074

Conventional catalysts such as Catalysts F, G and H are primarily used in cyclic reformer units where they are subjected to high severity operating conditions (low pressure and sometimes high moisture level in recycle gas). Under these conditions, the catalysts exhibit higher coking rates, i.e. rapid deactivation and require frequent (once every 1-2 weeks) regeneration. Catalysts B, C and D of the present invention will allow for significantly better yields and Activity stability and significant extension of the time on stream before the need for regeneration relative to conventional catalysts. In addition, in the rare cases when longer run length is not desired, catalysts of the present invention will allow for significant reduction of the coke-burn-off and reactor turnaround time thus again providing some longer unit uptime and higher profitability.

EXAMPLE 9

This example compares the performance of the steamed and oxychlorinated Catalysts D_{SO} and G_{SO} from Example 5.

The operating conditions and catalyst loadings were as described in Example 8. Figures 3 and 4 show the C_5+ yield and Activity decline curves, respectively, obtained in these tests. The test data show that Catalyst D_{SO} significantly outperformed conventional Catalyst G_{SO}, affording remarkably lower C_5+ yield and Activity decline rates, lower coke make rates and much higher C_5+ yield and Activity stability advantage than the one observed for fresh catalysts (see Example 8). This suggests that after very high unit moisture upset the Pt dispersion and the performance of Catalyst D of this invention will be much more readily restorable (via regeneration) than that of conventional Catalyst G.

EXAMPLE 10

This example compares the performance of a Pt- and Re-containing catalyst of the present invention (Catalyst I from Example 6) against conventional Pt- and Re-containing catalysts (Catalysts J, K and L from Example 7).

Samples of all four catalysts were used to catalyze the reforming of a full range commercial hydrotreated naphtha having a P/N/A content of 66/21/13 wt.%, respectively. The tests were conducted using the same equipment and under the same conditions as described in Example 8. Figures 5 and 6 show the C_5+ yield and reactor wall temperature (Activity decline) curves, respectively, for Catalysts I to L. Table 4 shows the corresponding Activity and C_5+ yield decline rates and coking rates.

The analysis of the data shows that Catalyst I of the present invention afforded significantly lower coking rates and lower C_5+ yields and activity decline rates; i.e., higher stability, relative to conventional Catalysts J to L. Thus, the data clearly show that the addition of the proper concentrations of both Bi and P to the supports of noble metal-containing catalysts results in a synergistic improvement in catalyst performance. It is obvious that Catalyst I of this invention will allow the refiner to operate at significantly lower temperatures while maintaining C_5+ yield and achieving the desired octane level (conversion). In addition, in this particular case, Catalyst I will allow for significant extension of the run length, i. e. increased unit uptime and profitability. Catalyst I will

also allow the refiner to increase profitability by increasing the unit throughput (feed space velocity) while still operating at acceptable reactor inlet temperatures, thereby producing more reformate with same octane per unit of time relative to the conventional catalyst systems. Catalyst I would be especially desirable for reformer units that are Activity limited.

Table 4

Ave. Hourly

Decline Rates

Catalyst	Pt/Re/Bi/P, wt.%	Activity, °C/hr.	C_5+ Yield, vol.%/hr.	Coking Rate, wt.%/hr.
I	0.25/0.26/0.06/0.3	+0.184	-0.016	+0.070
J	0.26/0.24/0.06/0	+0.284	-0.035	+0.076
K	0.25/0.25/0/0.3	+0.247	-0.020	+0.074
L	0.25/0.25/0/0	+0.281	-0.027	+0.075

CLAIMS

1. A catalyst support comprising γ-alumina particles throughout which a concentration of bismuth between 0.05 wt. % and 0.1 wt. % and a concentration of phosphorus between 0.05 wt. % and 0.6 wt. % have been essentially homogeneously distributed.

2. The catalyst support of claim 1 wherein the concentration of bismuth is between 0.05 wt. % and 0.1 wt. % and the concentration of phosphorus is between 0.1 wt. % and 0.4 wt. %.

3. The catalyst support of claim 1 wherein the concentration of bismuth is between 0.05 wt. % and 0.1 wt. % and the concentration of phosphorus is between 0.25 wt. % and 0.35 wt. %.

4. The catalyst support of claim 1 wherein the particles are extrudates.

5. A process for making a catalyst support comprising:

   a) preparing a solution comprising a bismuth precursor and a solution comprising a phosphorus precursor;

   b) preparing a mixture of γ-alumina and alumina sol;

   c) blending the mixture of step (b) with the solutions prepared in step (a), thereby making a support precursor having a concentration of bismuth between 0.05 wt. % and 0.1 wt. % and a concentration of phosphorus between 0.05 wt. % and 0.6 wt. % distributed essentially homogeneously throughout;

   d) forming the support precursor into particles; and

   e) drying and calcining the particles.

6. The process of claim 5 wherein the bismuth precursor is selected from the group consisting of $Bi(NO_3)_3$ $5H_2O$, $BiCl_3$, BiOCl, $BiBr_3$, Bi acetate, Bi citrate, and Bi alcoxides.

7. The process of claim 5 wherein the bismuth precursor is $Bi(NO_3)_3$ $5H_2O$.

8. The process of claim 5 wherein the phosphorus precursor is selected from the group consisting of H_3PO_4, H_3PO_3 H_3PO_2, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$.

9. The process of claim 5 wherein the phosphorus precursor is H_3PO_4.

10. The process of claim 5 wherein the mixture of γ-alumina and alumina sol comprises about 62 wt. % γ-alumina and the remainder alumina sol.

11. A naphtha reforming catalyst comprising the catalyst support of claim 1 and further comprising platinum in an amount between 0.1 wt. % and 1 wt. % of the catalyst and chlorine in an amount between 0.05 wt. % and 2 wt. % of the catalyst.

12. The catalyst of claim 11 further comprising an amount of rhenium between 0.01 wt. % and 1 wt. % .

13. The catalyst of claim 11 wherein the amount of platinum is between 0.15 wt. % and 0.6 wt. % of the catalyst and the amount of chlorine is between 0.8 wt. % and 1.2 wt. % of the catalyst.

14. The catalyst of claim 11 wherein the amount of platinum is between 0.2 wt. % and 0.3 wt. % of the catalyst and the amount of chlorine is between 0.9 wt. % and 1.1 wt. % of the catalyst.

15. The catalyst of claim 11 wherein the amount of platinum is between 0.15 wt. % and 0.6 wt. % of the catalyst and the amount of chlorine is between 0.8 wt. % and 1.2 wt. % of the catalyst, and wherein the catalyst further comprises between 0.1 wt. % and 0.5 wt. % of rhenium.

16. The catalyst of claim 11 wherein the amount of platinum is between 0.2 wt. % and 0.3 wt. % of the catalyst and the amount of chlorine is between 0.9 wt. % and 1.1 wt. % of the catalyst, and wherein the catalyst further comprises between 0.2 wt. % and 0.45 wt. % of rhenium.

17 The catalyst of claim 11 wherein:

the concentration of bismuth in the catalyst support is between 0.05 wt. % and 0.1 wt. % and the concentration of phosphorus in the catalyst support is between 0.25 wt. % and 0.35 wt. %; and

the amount of platinum is between 0.2 wt. % and 0.3 wt. % of the catalyst and the amount of chlorine is between 0.9 wt. % and 1.1 wt. % of the catalyst.

18. The catalyst of claim 11 wherein:

the concentration of bismuth in the catalyst support is between 0.05 wt. % and 0.1 wt. % and the concentration of phosphorus in the catalyst support is between 0.25 wt. % and 0.35 wt. %;

the amount of platinum is between 0.2 wt. % and 0.3 wt. % of the catalyst and the amount of chlorine is between 0.9 wt. % and 1.1 wt. % of the catalyst; and

the catalyst further comprises between 0.2 wt. % and 0.45 wt. % of rhenium.

19. A process for reforming hydrotreated naphtha comprising contacting said naphtha with the catalyst of claim 11 in the presence of hydrogen at elevated temperature and pressure.