

# **SPECIFICATION** **Reforming Process**

This invention relates to the joint use of zeolites with conventional reforming catalysts such as platinum or platinum-rhenium or multi-metallics on alumina.

5 Catalytic reforming of naphtha feed stocks has long been known in the petroleum industry. Most naphtha feeds contain large amounts of naphthenes and paraffins and consequently have low octane numbers. By means of various hydrocarbon conversion reactions, catalytic reforming has improved the octane number of naphtha feed stocks. Some of the more important conversion reactions that take place during catalytic reforming are dehydrogenation of naphthenes to aromatics, 10 dehydrocyclization of paraffins to naphthenes and aromatics and isomerization of normal paraffins to isoparaffins. A less desirable reaction that also occurs during reforming is the hydrocracking of long chain paraffins to gaseous hydrocarbons such as methane and ethane. 10

The above reforming reactions have previously been catalyzed by catalysts comprising porous supports, such as alumina, that have dehydrogenation promoting metal components impregnated or 15 admixed with the support. Platinum on alumina and, more recently, multimetallics, including bimetallics, such as platinum and rhenium on alumina, are examples of these catalysts. 15

Reforming catalysts should possess high selectivity, high activity and good stability. Selectivity in reforming is the ability of a catalyst to selectively produce high yield of high octane products, such as aromatics, from compounds that have relatively low octane numbers, such as 20 naphthenes and paraffins. The activity of a catalyst is the ability to convert the feed stock into all products without regard to selectivity. A stable catalyst is highly desirable so that the activity and selectivity characteristics of a catalyst can be maintained during prolonged periods of operation. 20

It is known in the art to admix certain zeolites with other catalytic materials. For instance, British Patent 1,056,493 discloses mixing together an alumina-supported platinum catalyst and a chabazite 25 zeolite and using it in a hydrocracking operation. British Patent 1,255,544 discloses a dual purpose catalyst comprising a zeolite, especially mordenite, having incorporated therein both platinum and rhenium. 25

U.S. 3,267,022 and U.S. 3,324,047 disclose composites of a zeolite having a pore size of from 6—14 Å and an adjuvant such as alumina. Hydrogenation activity is said to be imparted by adding, for 30 example, a Group VIII metal, either to the zeolite or to the adjuvant. The amount of zeolite is from 20—80% by weight. 30

U.S. 3,544,451 refers to a hydrocarbon conversion catalyst which comprises platinum and rhenium combined with a carrier material containing alumina and finely divided mordenite.

U.S. 3,702,886 discloses a composite of from 1—90% of a zeolite, such as ZSM-5, with a metal 35 oxide matrix material and a hydrogenation component. 35

U.S. 3,758,402 discloses the hydrocracking of hydrocarbons to motor fuel products by contacting a hydrocarbon charge with a catalytic mixture containing hydrogenation components, a large pore size zeolite such as zeolite X or Y and a smaller pore size zeolite such as ZSM-5 and a matrix material, an example of which is alumina. The zeolite components may comprise from 1—95% of the 40 final composite. 40

U.S. 3,365,392 discloses the catalytic reforming of gasoline charge stock to produce high octane reformate and LPG by contacting a charge with a catalyst comprising a platinum group metal on a support comprising a finely divided crystalline aluminosilicate suspended in an alumina matrix. The preferred aluminosilicate is the hydrogen or polyvalent form of mordenite.

45 U.S. 3,546,102 is concerned with a hydrocarbon conversion catalyst consisting essentially of a co-catalytic support and a Group VIII metal. The support contains an adsorbent refractory inorganic oxide and mordenite structure zeolite. The preferred metal is platinum, and it is incorporated into the zeolite-inorganic oxide blend after blending but before drying and calcining. 45

Other U.S. patents disclosing catalytic composites comprising platinum, or rhenium, or both, 50 optionally a matrix and mordenite as the sole or preferred crystalline aluminosilicate are 3,369,997, 3,376,214, 3,376,215, 3,464,929, 3,511,773, 3,523,914, 3,562,108 and 3,574,092. 50

We have now discovered that by judicious incorporation of a zeolite into the catalyst system of a reforming unit unexpectedly advantageous operation of the reforming process is achieved. In particular the catalyst system of this invention has the ability when compared to commercially available 55 reforming catalyst systems, to reduce the C<sub>1</sub> and C<sub>2</sub> concentrations in the effluent gas while increasing the C<sub>3</sub> and C<sub>4</sub> yields. This necessarily improves the selectivity of the catalyst and increases the yield of high octane products. The catalyst is also more active and much more resistant to aging than conventional reforming catalyst and give higher octane number products at given conditions. 55

In essence, the invention concerns the reforming of hydrocarbons by contacting same under 60 reforming conditions with a catalyst system in which the total catalyst comprises (1) from 1% to 100% of a composite comprising (a) an effective amount, from 0.1 to 25%, by weight of a crystalline zeolite selected from ZSM-5, ZSM-11, ZSM-35 and tetraethylammonium mordenite, (b) not less than 75% by weight, of a carrier material, (c) from 0.01% to 2%, by weight, of a platinum group metal either alone or in combination with other metals, and (d) from 0.01 to 3%, by weight, of a halide and (2) from 0% to 60

99% of a conventional reforming catalyst composition comprising (a) a carrier material, (b) from 0.01% to 2%, by weight, of a platinum group metal either alone or in combination with other metals, and (c) from 0.01% to 3%, by weight, of a halogen said total catalyst system having a K factor from 1.5 to 15; this factor being as defined later in the specification in equations 2 and 3. (2) above will be hereinafter sometimes referred to as "catalyst B".

The invention may thus be broadly viewed as the provision of a zeolite component in at least a portion of the catalyst constituting the inventory of a reforming unit. There is, of course, no requirement that the reforming catalyst which is supplemented by zeolite be identical with that which is not. Whilst many reforming catalysts are commercially available they all fall under the general designation "platinum-on-alumina".

The phrase "platinum on alumina" includes, for example, platinum, palladium, osmium, iridium, ruthenium, or rhodium and mixtures thereof with each other or with other metals, such as metals of Group VII-B, including rhenium, deposited on a suitable support. Generally, the major portion of the conventional reforming catalyst will be alumina, which may comprise as much as 99% by weight or more of these composites. Other components may be combined with the alumina carrier, such as oxides of silicon, magnesium, zirconium, thorium, vanadium, titanium, boron or mixtures thereof. The platinum-alumina combination, either with or without one or more of the above listed components such as silica, is also promoted with small amounts of halogen such as chlorine and fluorine in amounts ranging from 0.01% up to 3% by weight; less than 3% of halogen being employed with the standard platinum group composite. In a preferred embodiment, the carrier material is a relatively high surface area material, preferably an eta-alumina or gamma-alumina material or mixtures thereof having a surface area of at least 100 square meters per gram. Preparation of the reforming catalyst may be accomplished by different procedures described in the prior art. In one procedure an alumina carrier material is impregnated with the acid or salt of one or more of the herein described hydrogenating components in amounts that will produce 0.01% up to 2% by weight of the metal, but generally not more than 0.6% by weight of platinum is employed.

A naturally occurring or a synthetically prepared alumina with or without silica may be employed as a carrier material or support. Preferably, supports are high surface area material such as a base alumina as discussed above. Before use, the high surface area platinum-containing composites may be reduced in a hydrogen atmosphere and maintained preferably in a substantially moisture-free atmosphere before being put on stream.

In preparation of the zeolite-containing reforming catalyst not less than 75% of zeolite-free reforming catalyst is mixed with 0.1 to 25%, preferably 0.1 to 15% by wt of zeolite. The more preferred concentration of zeolite is 0.1 to 5% or 10%, intimately mixed with the conventional reforming catalyst under conditions such that the average particle size of the zeolite is not more than 10 microns. These percentages are based on the combined weight of conventional reforming catalyst and zeolite. The exact amount of zeolite that is mixed with the platinum-metal on alumina component depends upon the K factor described hereinbelow and the pretreatment conditions, both of which are directly concerned with the activity of the zeolite catalyst.

The activity and aging characteristics of reformer systems are remarkably controlled by catalyst composites of this invention which are prepared with regulated degrees of acidity. Because catalyst composites of this invention have higher acidities than conventional reforming catalysts, the acidity of the total reformer system, containing zeolite composites in either all or part of the total reformer, will be greater than for conventional systems. The acidity of the total reformer catalyst system, when properly controlled gave balanced activity and aging characteristics when the K factor was not less than 1.5 and not greater than 15. The K factor for a total reformer system is defined as a function of the rate at which all catalysts in the system isomerize o-xylene to m- and p-xylenes compared to that at which a standard reforming catalyst (minus any zeolite) isomerizes o-xylene under the same condition. Further the "Relative Activity" for a given composite is defined as the rate at which the composite isomerizes o-xylene to m- and p-xylenes compared to that at which the standard reforming catalyst minus any zeolite isomerizes o-xylene under the same conditions.

Isomerization activities of these composites were measured in an isothermal downflow tubular glass reactor at atmospheric pressure. The reactor bed of approximately 0.5 grams of 14x25 mesh pre-reduced particles was preceded by a preheat section containing 3 cc of 8/10 mesh quartz chips. (Here and hereinafter in this specification the reference to mesh size refers to Tyler mesh). The preheat and catalyst bed sections were both maintained at the same temperature. The catalyst was heated to 1000°F at a rate of 10°F per minute in a 100 cc per minute hydrogen flow. After one hour hydrogen addition was discontinued and the catalyst cooled to 900°F with a helium purge. At 900°F the purge was stopped and ortho xylene added at a rate of  $2.5 \pm 0.5$  grams per gram of catalyst per hour. Liquid reactor effluent was collected and analyzed by gas chromatography. The conversion of ortho xylene to meta plus para xylenes was calculated per one-half gram of catalyst. The % conversion of the o-xylene per one-half gram of the standard catalyst under these reaction conditions is 1.1%. The catalytic rate constants for conversion of ortho xylene to meta xylene and para xylene relative to that for an equal weight of the standard commercial platinum-rhenium catalyst were determined by the following equation for the liquid effluent collected between 50 and 70 minutes on stream.

$$\text{Relative Activity} = \frac{\log(1-X_e) - \log(X-X_e)}{\log(1-X_e) - \log(Y-X_e)} \quad (1)$$

where

$X_e$  = concentration of o-xylene at equilibrium,

5  $X$  = ortho xylene concentration in the liquid product from one-half gram of the experimental catalyst and

$Y$  = the ortho xylene concentration given at the same conditions by one-half gram of the standard catalyst (R16H). All concentrations are in mole fractions.

This is a first order rate equation for a reaction which can proceed to equilibrium.

10 At the standard temperature of 900°F the value of  $X_e = 0.25$  and with the specified standard the value of  $Y$  was found to be 0.989 so the equation reduces to

$$\text{Relative Activity} = \frac{9.8751 - 10 - \log(X - 0.25)}{0.0065} \quad (2)$$

Thus for the purposes of this disclosure the term "standard reforming catalyst" shall mean a specific commercially available reforming catalyst containing 0.37% Pt and 0.20% Re and 0.9% chloride impregnated on gamma alumina (see Example 7) which gives an o-xylene conversion of 1.1% per 0.5 grams at the above specified test conditions.

The K factor hereinabove referred to is defined as:

$$\text{K factor} = (\text{Relative Activity of Zeolite Composite}) \times (\text{Vol. fraction of Zeolite Composite}) + (\text{Relative Activity of Non-Zeolite Composite}) \times (\text{Vol. fraction of Non-Zeolite Composite}). \quad (3)$$

20 In practice K can range from 1.5 to 15. Preferably, it will range from 1.5 to 10, more preferably from 2 to 5.

When the K factor is 1.5 to 15 the mixed zeolite-reforming catalysts show significant improvement in stability toward aging during reforming, while still maintaining high liquid yields at high octane number. When the K factor is below 1.5, the catalyst in reforming reactions deteriorates rapidly to a point of inactivity. When the K factor is above 15 the catalyst system is too highly acidic to give optimum liquid reformat yields ( $C_5+$ ) along with the desired resistance to aging:  $C_3+$  yields are high, but high octane liquid yields are low.

25 The K factor is thus a measure of the acidity, and thus the activity, of the zeolite. Various techniques can be used to control the degree of acidity of the zeolite-containing composite. One technique is to treat the zeolite, either before or after mixing with the platinum metal-alumina component, with air or steam at elevated temperatures e.g. up to 1700°F in air or at from 800°F to 1700°F in steam. It may also be controlled by adding alkali or alkaline earth metals or metal cations to the zeolite, again before or after compositing with the platinum-metal alumina base. Another way is to reduce the alumina content of the zeolite so that the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio increases and the cation content decreases. A final illustration is the control of the zeolite content so that the desired degree of acidity is obtained.

35 The zeolites that are used in the practice of the present invention are tetraethylammonium (TEA) mordenite, ZSM-5 (described in U.S. 3,702,886), ZSM-11 (described in U.S. 3,709,979) and ZSM-35 (described in U.S. 4,016,245).

40 Reforming according to the invention may advantageously be conducted at 0.5 to 50 WHSV, 800 to 1050°F, 85 to 500 psig pressure and 1 to 10 molar ratio of hydrogen to hydrocarbons. Preferably the WHSV is 1 to 20. Usually a plurality of reactors is employed, and the zeolite-containing catalyst may be employed in any or all of them, particularly in the last.

45 The zeolite containing composite may be prepared by pre-milling a conventional reforming catalyst alone in a ball mill for 24 hours, mixing the premilled composition with the zeolite and ballmilling for two hours, followed by pelleting. Other methods of compositing are also useful. For example, the zeolite may be added to alumina sols or slurries either before or after a Pt metal is added.

In preparing the zeolitic composite the proper balance between the amount of zeolitic component and the conventional reforming catalyst component will depend upon the charge stock and operating conditions. However, it should be noted that one of the advantages of this invention lies in the degree of activity with attendant stability, that the zeolitic component possesses. This high activity, while usefully high up to sizes of 10 microns, will be highest when crystallites are less than 2 microns in size, preferably less than 1 micron, in weight mean particle diameter, and allows for an appreciable degree of flexibility in both catalyst composition and operating conditions (including in this regard materials normally thought of as inhibitors in the reforming process, such as nitrogen and sulfur containing compounds).

55 Generally ion exchange, washing, calcination, steaming and other such operations performed on

the zeolite should be carried out prior to combining with the carrier material. Admixture of the zeolite with the conventional reforming catalyst may be accomplished by physically mixing the same either directly or after compositing in a matrix.

When the zeolitic catalyst and conventional reforming catalyst are mixed as large particles, for example, greater than 40 mesh, the zeolite may be dispersed in a hydrous oxide matrix such as silica, alumina, magnesia and clay. Generally, the amount of zeolite will fall within the range of from 1% to 70% by weight of the zeolite-matrix system.

Additionally, the platinum type metal may be added to the zeolite, either before or after admixture thereof with a matrix. When the composite comprises an intimate mixture of zeolite and conventional reforming catalyst, the platinum type metal may be combined with the alumina, either before or after incorporation of the zeolite.

In all these various embodiments, the product aging is diminished and the selectivity is substantially changed at a given octane number from that given by the conventional reforming catalyst alone at the same octane severity. In all cases the gaseous products contain more  $C_3$  and  $C_4$  than  $C_1$  and  $C_2$ . Further, the operating severity needed to reach a given octane number is less for the combination catalyst of this invention than the reforming catalyst alone.

The naphtha charge stocks which can be reformed over the catalysts of this invention include typical reforming stocks, namely virgin naphthas, cracked naphthas and partially reformed naphthas.

The following Examples will illustrate the advantages of the catalyst of this invention.

#### Example 1

The hydrogen form of zeolite ZSM-5 was composited with a commercial reforming catalyst containing 0.35 wt.% Pt and 0.35% chloride on an eta-alumina base (RD 150 C as manufactured by Engelhard Mineral and Chemical Company). Compositing was achieved by ballmilling for two hours. The conventional reforming catalyst was pre-milled alone in a ball mill for 24 hours prior to compositing with the HZSM-5. The final composite was pelleted by slugging to form 1/2" diameter pellets which were crushed to 14 to 25 mesh. These particles had an apparent density of 0.76 g/cc and a Relative Activity value of 46.5.

The reforming activity of this composite, referred to as the catalyst of Example 1, was tested with a pretreated  $C_6$ -330°F Kuwait naphtha as the charge stock (see Table 4). The results of this test are summarized in Table 5. The conditions of the run are shown in the table. This catalyst, which contains 10% HZSM-5 (by weight) produced 37.7%  $C_6^+$  liquid product at an aromatic level of 80.2 weight percent for the 12 liquid hourly space velocity, (LHSV) run. At 50 LHSV the  $C_6^+$  product has increased to 56.9% and the aromatics level approached 50%, with excellent gaseous product distribution. Thus this catalyst system, which has a K value of 46.5, is useful not for conventional reforming but for producing high yields of  $C_3$ 's and  $C_4$ 's along with high octane gasoline.

#### Example 2

A composite which contained 10% (by weight) of HZSM-5 was prepared using the same materials and techniques as described in Example 1 except that the HZSM-5 was steamed for 20 hours at 1225°F with 100% steam at atmospheric pressure prior to compositing. The final composite in 14 to 25 mesh size had an apparent density of 0.73 g/cc and a Relative Activity value of 31.1.

The reforming activity of this composite was also tested with a pretreated  $C_6$ -330°F Kuwait naphtha (Table 4) as the charge stock. The results of this test with this composite again occupying the entire reforming reactor are summarized in Table 5. The K factor for this system was of course 31.1. As in Example 1, the catalyst system is useful not for conventional reforming but for producing high yields of  $C_3$ 's and  $C_4$ 's along with high octane gasoline.

#### Example 3

The upstream 90 volume percent of the catalyst bed of a reformer reactor was stocked with 3.5 cc of commercial platinum-rhenium on alumina reforming catalyst, the downstream 10 volume % with 0.5 cc of the composite prepared in Example 2. The total catalyst system had a K factor of 4.0 and was tested for reforming activity with the pretreated  $C_6$ -330°F Kuwait Naphtha of Table 4. The conditions and results are shown in Table 6 together with the results obtained with the commercial catalyst occupying the entire reactor. At both 900 and 920°F more liquid product was obtained than in Example 1 or Example 2, and the gas distribution was vastly superior to the product distributions obtained with the commercial bi-metallic platinum-rhenium-alumina alone at 940°F.

(15)

**Table 4**  
**Physical Properties of Hydrodesulfurized**  
**Reforming Naphtha Feed<sup>1</sup>**

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|---|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|----|

<sup>1</sup>Naphthas referred to herein were pretreated with pure hydrogen at 500 psig, 700°F, 5 LHSV over a commercial cobalt molybdena hydrotreating catalyst.

**Table 5**

**C<sub>6</sub>-330°F Kuwait Naphtha Reforming Over HZSM-5/pt/Al<sub>2</sub>O<sub>3</sub>**

| 25 | Catalyst                                  | Fresh Catalyst of Example 1 |        |        | Steamed Catalyst of Example 2 |       |       | 25 |
|----|-------------------------------------------|-----------------------------|--------|--------|-------------------------------|-------|-------|----|
|    |                                           | 900                         | 900    | 900    | 900                           | 900   | 950   |    |
|    | Temp. °F                                  |                             |        |        |                               |       |       |    |
| 30 | LHSV (vol. Liq. per<br>vol. cat. per hr.) | 12                          | 50     | 50     | 50                            | 12    | 12    | 30 |
|    | Pressure (psig)                           | 200                         | 200    | 200    | 200                           | 200   | 200   |    |
|    | Hours on Stream                           | 4.5                         | 5      | 24     | 5                             | 5     | 10    |    |
|    | Weight Charge, grams                      | 2.19                        | 2.19   | 2.19   | 2.19                          | 2.19  | 2.19  |    |
| 35 | Weight Product, grams                     | 2.04                        | 2.07   | 2.12   | 2.09                          | 2.16  | 1.91  |    |
|    | Liquid, grams                             | 0.81                        | 1.19   | 1.23   | 1.90                          | 1.60  | 1.26  | 35 |
|    | Gas, grams                                | 1.23                        | 0.88   | 0.89   | 0.19                          | 0.56  | 0.64  |    |
|    | Wt.% Recovery                             | 93.4                        | 94.5   | 97.0   | 95.8                          | 98.6  | 87.3  |    |
|    | Wt.% C <sub>5</sub> <sup>+</sup>          | 37.7                        | 55.1   | 56.9   | 87.0                          | 73.7  | 58.9  |    |
| 40 | Wt.% C <sub>4</sub> <sup>-</sup>          | 55.8                        | 39.4   | 40.1   | 8.8                           | 24.9  | 23.4  |    |
|    | Wt.% Arom. in C <sub>5</sub> <sup>+</sup> | 80.2                        | 49.9   | 48.2   | 33.3                          | 46.0  | 55.2  | 40 |
|    | Gas Composition, Wt.%                     |                             |        |        |                               |       |       |    |
|    | C <sub>1</sub>                            | 1.6                         | 0.8    | 0.7    | 1.7                           | 1.4   | 0.9   |    |
|    | C <sub>2</sub>                            | 11.4                        | 6.6    | 7.0    | 7.2                           | 4.3   | 9.2   |    |
| 45 | C <sub>3</sub>                            | 66.7                        | 66.7   | 67.5   | 69.8                          | 62.5  | 72.1  |    |
|    | C <sub>4</sub>                            | 19.2                        | 24.1   | 23.1   | 20.2                          | 29.8  | 15.3  | 45 |
|    | C <sub>5</sub>                            | 1.1                         | 1.7    | 1.6    | 1.1                           | 1.9   | 2.6   |    |
|    | Cat. Vol. (cc)                            | 0.55cc                      | 0.12cc | 0.12cc | 0.12cc                        | 0.5cc | 0.5cc |    |

Table 6

|    |                                | Commercial Catalyst <sup>(2)</sup><br>Pt/Re/Al <sub>2</sub> O <sub>3</sub> |      | Example 3 |      |    |
|----|--------------------------------|----------------------------------------------------------------------------|------|-----------|------|----|
| 5  | Catalyst Temp. °F              | 940                                                                        | 940  | 920       | 900  | 5  |
|    | LHSV                           | 1.5                                                                        | 1.5  | 1.5       | 1.5  |    |
|    | Pressure, psig                 | 200                                                                        | 200  | 200       | 200  |    |
|    | Hours on Stream                | 22                                                                         | 45   | 5         | 24   |    |
|    | Weight Charge, grams           | —                                                                          | 2.19 | 2.19      | 2.19 |    |
| 10 | Weight Product, grams          | —                                                                          | 2.01 | 2.06      | 2.17 | 10 |
|    | Liquid, grams                  | —                                                                          | 1.49 | 1.37      | 1.48 |    |
|    | Gas, grams                     | —                                                                          | 0.52 | 0.69      | 0.69 |    |
|    | Wt.% Recovery                  | —                                                                          | 91.8 | 94.2      | 96.4 |    |
|    | Wt.% C <sub>5</sub> +          | —                                                                          | 68.4 | 63.3      | 66.5 |    |
| 15 | Wt.% C <sub>4</sub> —          | —                                                                          | 23.4 | 30.9      | 29.9 | 15 |
|    | Wt.% Arom. in C <sub>5</sub> + | 62.8                                                                       | 54.6 | 62.2      | 63.6 |    |
|    | Gas Composition, Wt.%          |                                                                            |      |           |      |    |
|    | C <sub>1</sub>                 | 15.4                                                                       | 9.8  | 5.9       | 0.6  |    |
|    | C <sub>2</sub>                 | 45.4                                                                       | 32.3 | 14.8      | 5.1  |    |
| 20 | C <sub>3</sub>                 | 32.6                                                                       | 40.9 | 51.7      | 63.8 | 20 |
|    | C <sub>4</sub>                 | 6.3                                                                        | 15.9 | 25.4      | 27.9 |    |
|    | C <sub>5</sub>                 | 0.3                                                                        | 1.1  | 2.0       | 2.5  |    |
|    | Cat. Vol. (cc)                 |                                                                            |      | 4.0cc     |      |    |

## Example 4

- 25 HZSM-5 was calcined for 10 hours at 1000°F, steamed at 1225°F for 24 hours with 100% steam at atmospheric pressure, and then composited with ballmilled commercial 0.35 wt.% Pt on eta-alumina as described in Example 1, the relative quantities being such as to give 1% HZSM-5 in the final composite. The final composite, pelleted and sized 14 to 25 mesh, had an apparent density of 0.70 g/cc and a Relative Activity value of 3.4. 25
- 30 The reforming activity of this catalyst composite, occupying the entire reactor, was tested using the C<sub>6</sub>-330°F Kuwait Naphtha in Table 4 as a charge stock. The K value was 3.4, the same as the Relative Activity value. The conditions of the run and the results are shown in Table 7. These results indicate that even at extremely low levels of intimately mixed HZSM-5 the combined C<sub>3</sub>—C<sub>4</sub> concentration in the gas product is 80% or greater. Even when the pressure was lowered to 100 psig, no apparent effect was observed on product distribution. Additionally, this catalyst showed no indication of aging during the course of operation. 35

Table 7

| C <sub>6</sub> -330°F Kuwait Naphtha Reforming With Steamed 1% HZSM-5-99% (0.35 Pt/nAl <sub>2</sub> O <sub>3</sub> ) <sup>(1)</sup> |                                                                                                   |      |      |      |      |      |      |       |         |      |
|-------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|------|------|------|------|------|------|-------|---------|------|
| 40                                                                                                                                  | Catalyst: Example 3; H <sub>2</sub> /HC 7/1; Charge: C <sub>6</sub> -330 Kuwait Naphtha; LHSV 1.5 |      |      |      |      |      |      |       |         |      |
|                                                                                                                                     | Temp. °F (920°F)                                                                                  | 918  | 916  | 917  | 917  | 917  | 918  | 918   | 918     | 916  |
|                                                                                                                                     | LHSV <sup>(2)</sup>                                                                               | 1.5  |      |      |      |      |      |       |         |      |
|                                                                                                                                     | Pressure (psig)                                                                                   | 200  |      |      |      |      |      |       | 200/100 | 100  |
|                                                                                                                                     | Hours on Stream                                                                                   | 4    | 12   | 32   | 35   | 55   | 59   | 83    | 103     | 108  |
| 45                                                                                                                                  | Weight Charge, grams                                                                              | 2.18 | 2.19 | 2.19 | 2.20 | 2.20 | 2.21 | 2.22  | 2.22    | 2.23 |
|                                                                                                                                     | Weight Product, grams                                                                             | 1.16 | 1.80 | 1.80 | 1.92 | 2.01 | 1.68 | 2.23  | 1.98    | 2.08 |
|                                                                                                                                     | Liquid, grams                                                                                     | 0.71 | 1.14 | 1.19 | 1.26 | 1.39 | 1.28 | 1.41  | 1.26    | 1.39 |
|                                                                                                                                     | Gas, grams                                                                                        | 0.45 | 0.66 | 0.61 | 0.66 | 0.61 | 0.40 | 0.82  | 0.72    | 0.69 |
|                                                                                                                                     | Wt.% Recovery                                                                                     | 53.1 | 82.3 | 82.2 | 87.2 | 91.2 | 76.1 | 100.1 | 89.1    | 93.4 |
| 50                                                                                                                                  | Wt.% C <sub>5</sub> +                                                                             | 32.7 | 52.6 | 54.7 | 57.9 | 63.7 | 57.9 | 64.3  | 57.2    | 63.0 |
|                                                                                                                                     | Wt.% C <sub>4</sub> —                                                                             | 20.4 | 29.7 | 27.5 | 29.3 | 27.4 | 18.2 | 25.8  | 31.8    | 30.3 |
|                                                                                                                                     | Wt.% Arom. in C <sub>5</sub> +                                                                    | 74.1 | 66.8 | 62.8 | 63.8 | 62.4 | 60.2 | 61.3  | 57.9    | 62.1 |
|                                                                                                                                     | Gas Composition, wt.%                                                                             |      |      |      |      |      |      |       |         |      |
| 55                                                                                                                                  | C <sub>1</sub>                                                                                    | 5.4  | 4.1  | 4.1  | 2.2  | 4.5  | 4.3  | 3.3   | 3.0     | 3.3  |
|                                                                                                                                     | C <sub>2</sub>                                                                                    | 20.8 | 15.6 | 14.1 | 10.2 | 12.4 | 15.2 | 11.6  | 9.9     | 10.2 |
|                                                                                                                                     | C <sub>3</sub>                                                                                    | 58.3 | 58.6 | 55.5 | 54.9 | 55.7 | 59.8 | 52.7  | 54.6    | 54.4 |
|                                                                                                                                     | C <sub>4</sub>                                                                                    | 14.9 | 20.3 | 24.8 | 30.1 | 25.6 | 19.7 | 29.8  | 30.2    | 39.8 |
|                                                                                                                                     | C <sub>5</sub>                                                                                    | 0.6  | 1.4  | 1.6  | 2.6  | 1.8  | 0.8  | 2.6   | 2.3     | 2.3  |

(1) For properties of charge stock see Table 4.

(2) Catalyst: 4.0 cc, 2.85 g.

**Example 5**

The composite of Example 4, occupying the entire reactor, was tested for its reforming activity with a C<sub>6</sub>-290°F Mid-Continent naphtha (see Table 4) under conditions shown in Table 8. The K factor for this catalyst was 3.4. The results are compared with a standard commercial 0.6 wt.% platinum on alumina in Table 8. At 905°F, the catalyst shows a C<sub>5</sub><sup>+</sup> clear research octane gain of 7.3 units over the standard 0.6 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> (101.8 versus 94.5). The comparison of these two catalysts at more nearly the same octane level (standard Pt/Al<sub>2</sub>O<sub>3</sub> at 905°F, catalyst of Example 3 at 870°F) shows more than a 35°F advantage for the HZSM-5 catalyst over the standard.

The gaseous product distributions at the 94.5/96.4 octane level for the liquid product show a decrease in C<sub>1</sub>+C<sub>2</sub> yield with a corresponding increase in C<sub>3</sub> and C<sub>4</sub> yields. In the C<sub>4</sub> isomer fraction, the isomer distribution shows isobutane yield is greater than normal butane yield for the ZSM-5 composite of Example 4, whereas for the standard Pt/Al<sub>2</sub>O<sub>3</sub> this ratio is reversed.

**Table 8**  
**C<sub>6</sub>-290 Mid-Continent Naphtha Reforming<sup>1</sup>**

|    | Catalyst                              | 0.6 wt.% Pt/Al <sub>2</sub> O <sub>3</sub> | Example 5 | Example 5 |    |
|----|---------------------------------------|--------------------------------------------|-----------|-----------|----|
| 15 | Pressure (psia)                       | 200                                        | 200       | 200       | 15 |
|    | Moles H <sub>2</sub> /mole HC         | 9.6                                        | 9.6       | 9.6       |    |
|    | LHSV                                  | 1.7                                        | 1.7       | 1.7       |    |
|    | Temperature °F                        | 905                                        | 905       | 870       |    |
| 20 | C <sub>5</sub> <sup>+</sup> RNO+O     | 94.5                                       | 101.8     | 96.4      | 20 |
|    | C <sub>1</sub> +C <sub>2</sub> (wt.%) | 1.8                                        | 3.0       | 1.6       |    |
|    | C <sub>3</sub> (wt.%)                 | 2.4                                        | 9.1       | 7.7       |    |
|    | iC <sub>4</sub> (wt.%)                | 1.3                                        | 5.7       | 5.5       |    |
|    | nC <sub>4</sub> (wt.%)                | 1.6                                        | 4.1       | 3.6       |    |
| 25 | C <sub>5</sub> <sup>+</sup> (vol.%)   | 83.4                                       | 69.7      | 74.4      | 25 |
|    | C <sub>4</sub> <sup>+</sup> (vol.%)   | 87.1                                       | 82.3      | 85.9      |    |

<sup>1</sup>Properties of naphtha charge in Table 4.

**Example 6**

6.4 cc of the composite of Example 4 was located downstream of 18.6 cc of a commercial conventional reforming catalyst containing 0.6 wt.% Pt on eta-Al<sub>2</sub>O<sub>3</sub> in a reforming test reactor. This reactor load, having a K factor of 2.5, was placed in an isothermal reforming test unit and evaluated for its activity toward reforming the C<sub>6</sub>-290°F Mid-Continent naphtha characterized in Table 4. This activity is compared with the standard Pt/Al<sub>2</sub>O<sub>3</sub> under identical test conditions as shown in Table 9 along with the results. The 2.5 K reactor loading furnished a C<sub>5</sub><sup>+</sup> liquid product having an octane number 2.6 units higher than that of the product from the standard Pt/Al<sub>2</sub>O<sub>3</sub>. Furthermore, this was accomplished with a loss of only 4% C<sub>5</sub><sup>+</sup> yield and only 1.5% C<sub>4</sub><sup>+</sup> yield. The net C<sub>1</sub>+C<sub>2</sub> yield for the catalyst herein claimed was less than from the standard (2.1 versus 2.3 wt. percent based on charge). Therefore, if the standard Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was run at increased severity (e.g. higher temperature) to give the same octane number level for the liquid product, the yield of methane plus ethane would be substantially greater than for the HZSM-5 catalyst composite. This is a very desirable catalytic property, since it leads to higher hydrogen purity in operations using recycle gas. The gain in C<sub>3</sub> and C<sub>4</sub> yield at the expense of C<sub>1</sub>+C<sub>2</sub> is also a very desirable result.

**Table 9**  
**Advantage of Split Bed-HZSM-5 Contained in Pt/Al<sub>2</sub>O<sub>3</sub>**  
**In Reforming a C<sub>6</sub>-290°F Mid-Continent Naphtha<sup>(1)</sup>**

|    | Catalyst                                        | Standard Pt/Al <sub>2</sub> O <sub>3</sub> | Example 6 |    |
|----|-------------------------------------------------|--------------------------------------------|-----------|----|
| 45 | Hydrogen/Hydrocarbon (mol/mol)                  | 4                                          | 4         | 45 |
|    | Vol. Chg/Vol. Cat/Hr                            | 1.7                                        | 1.7       |    |
| 50 | Pressure, psia                                  | 200                                        | 200       | 50 |
|    | Temperature                                     | 900                                        | 900       |    |
|    | Product Properties                              |                                            |           |    |
|    | C <sub>5</sub> <sup>+</sup> Res. Octane (clear) | 95.3                                       | 97.9      |    |
|    | C <sub>5</sub> <sup>+</sup> vol. Yield          | 82.6                                       | 78.6      |    |
| 55 | C <sub>4</sub> <sup>+</sup> vol. Yield          | 87.2                                       | 85.7      | 55 |
|    | C <sub>1</sub> +C <sub>2</sub> wt.% of Charge   | 2.3                                        | 2.1       |    |
|    | C <sub>3</sub>                                  | 3.1                                        | 5.1       |    |
|    | iC <sub>4</sub>                                 | 1.7                                        | 3.1       |    |
|    | nC <sub>4</sub>                                 | 1.9                                        | 2.5       |    |

**Example 7**

A commercially available conventional reforming catalyst containing 0.37 wt.% platinum, 0.20 wt.% rhenium and 0.9% chloride impregnated on a gamma alumina support was tested for catalytic stability by the following method. Twenty milliliters (20 ml) of the catalyst was loaded into a downflow isothermal reforming reactor. The reactor was heated to 960°F under a flow of pure hydrogen (40 liters/hour) at 150 psig. The temperature was lowered to 850°F, pure hydrogen addition stopped and a gaseous mixture of hydrogen sulfide in hydrogen (40 ppm H<sub>2</sub>S in hydrogen) was passed over the catalyst until hydrogen sulfide was detected in the exit gas. The H<sub>2</sub>S/H<sub>2</sub> mixture was discontinued and pure hydrogen started at a flow rate of 40.2 liters/hr. Liquid charge stock was pumped into the reactor at a rate of 36 milliliters per hour. The charge stock used here was a hydrogen pretreated C<sub>6</sub>-330°F Arabian light naphtha with the properties shown in Table 10. Temperature was increased to 900°F and held for one hour. Final temperature adjustment was made.

Temperature was chosen here and in subsequent examples to give at the start of the run a C<sub>8</sub><sup>+</sup> liquid product having a clear research octane number of 100±1.5 octane, which for this catalyst was 960°F.

In this aging stability evaluation the average decline in octane number of C<sub>8</sub><sup>+</sup> liquid product per day over the course of the run was 0.75 octane number per day. This is the average drop over a 16 day run in which the octane number declined from 99.7 on the first day to 88.7 on the 16th day. Periodic octane numbers were taken during the runs. C<sub>8</sub><sup>+</sup> volume liquid yield for this catalyst at the start of the run was 73%. C<sub>3</sub><sup>+</sup> volume yield was 90%.

Since this is the standard catalyst against which our experimental catalysts were rated for K, by definition K was 1.0.

**Table 10****Charge Stock: C<sub>6</sub>-330°F. Arabian Light Naphtha**

| Wt. %            | Properties |
|------------------|------------|
| Paraffins        | 68.8       |
| Naphthenes       | 18.4       |
| Aromatics        | 12.7       |
| Specific Gravity | API 63.0   |

**ASTM Distillation, °F**

|     |     |
|-----|-----|
| IBP | 168 |
| 10% | 199 |
| 30% | 218 |
| 50% | 241 |
| 70% | 268 |
| 90% | 296 |
| EP  | 322 |

|                         |       |
|-------------------------|-------|
| Clear Research Octane   | 37.8  |
| Avg. Mol. Wt.           | 106.4 |
| Wt. % Combined Hydrogen | 14.8  |

**Run Conditions were:**

- 150 psig total inlet pressure
- 7 moles of hydrogen feed per mole of hydrocarbon feed
- 1.8 volumes of charge stock per volume of catalyst per hour.

**Example 8**

Calcined HZSM-5 was steamed at 1100°F and composited with the commercial reforming catalyst described in Example 4 to yield a composite containing 1% by weight of HZSM-5.

This steamed HZSM-5 (1.298 grams) was mixed with 243.5 grams of hydrated commercial alumina-monohydrate (50.75% solids, obtained from Continental Oil Co.) in a muller mixer with 25 ml of water for 30 minutes. This mixture was extruded as 1/32" diameter particles, dried 4 hours at 230°F and heated to 1000°F at a rate of 2°F/minute and held for 10 hours.

A portion of the above extrudate (88.7 g, 99.7% solids) was placed in an evacuation chamber for 30 minutes and impregnated with 70.6 ml of an aqueous solution which contained 0.338 grams of platinum as hexachloroplatinic acid, 0.338 grams of rhenium as perrhenic acid and 0.456 grams of chloride as hydrochloric acid. After impregnation the extrudate stood for one hour at atmospheric pressure and was then dried at 230°F for 3 1/2 hours. The dried extrudate was calcined for 3 hours at 1000°F.

The final catalyst composite contained 0.44 wt.% platinum and 0.83% chlorine and had a surface area of 202 square meters per gram.

The Relative Activity factor for the composite of this example as defined by the o-xylene isomerization test was 6.4.

**Example 9**

The composite catalyst of Example 8 was evaluated for aging stability by the method discussed in Example 7 except that the catalyst bed differed. The top of the catalyst bed contained 8 cubic centimeters of the commercial Pt-Re/gamma alumina of Example 7 and bottom 12 cc of the bed was the composite of Example 8. The K factor for this total catalyst system was 4.2. All other conditions of the test were the same except that the temperature needed to reach the desired O.N. was 940°F. This shows the great increase in activity of this catalyst. The average octane number decline during the course of this run was 0.43 octane numbers per day.

The decline in aging rate in this catalyst was 43% less than the aging rate of the standard catalyst of Example 6 when tested under comparable conditions. Further, the activity is greater since a lower temperature was necessary to give a C<sub>8</sub><sup>+</sup> liquid product having a 100 clear research octane number. The C<sub>8</sub><sup>+</sup> liquid yield at the start of the run was 69 volume%. The C<sub>3</sub><sup>+</sup> yield was 95 volume%.

**Example 10**

A composite catalyst was prepared which contained one wt.% steamed HZSM-5 and 99 wt.% of the conventional reforming catalyst from Example 7. The steamed HZSM-5 was prepared by the method indicated in Example 8. The Pt-Re on alumina material of Example 7 was ball-milled 24 hours prior to using. The composite catalyst of this example was an intimate mixture of 0.90 grams of the HZSM-5 prepared in Example 7 and 90.0 grams of the Pt-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of Example 7. The composite was mixed for 2 minutes in an electric mixer and then ballmilled for one hour. The powder mixture was pelleted and sized to 14/25 mesh particles.

This composite catalyst had a relative activity of 5.2 and was evaluated by the method described in Example 7. The catalyst bed consisted of 8.0 cc of the conventional reforming catalyst of Example 7 in the top of the reactor and 12.0 cc of the composite of this example in the bottom of the bed. The K factor of this total catalyst system was 3.5. The temperature of this test was 930°F. Thus, this catalyst also is much more active than the standard catalyst of Example 7. The C<sub>8</sub><sup>+</sup> liquid yield at the start of the run was 70 volume%. The C<sub>3</sub><sup>+</sup> yield was 100 volume%. The octane decline rate of the dual catalyst system described here was 0.31 octanes per day. Its stability is far better than that of the conventional reforming catalyst described in Example 6 which declined at the higher rate of 0.75 octanes/day. The decline in aging rate compared to the standard conventional reforming catalyst (Example 7) is 59%.

**Example 11**

The composite of Example 4 was evaluated by the method described in Example 7. The catalyst bed contained 8.0 cc of the composite of Example 7 in the top of the bed and 12.0 cc of the catalyst of Example 4 in the bottom of the bed. This system had a K factor of 2.4. The temperature of this test was 930°F, again showing the increased catalyst activity. The average octane decline for this test was 0.37 octanes per day which is much less than the decline for the conventional reforming catalyst of Example 7. The decline in aging rate was 51% of the decline rate for the standard reforming catalyst of Example 7. The C<sub>8</sub><sup>+</sup> yield was 73 volume%. The C<sub>3</sub><sup>+</sup> yield was 96 volume%.

**Example 12**

The composite of this example was prepared by mixing 10 wt.% steamed hydrogen-form TEA mordenite with 90 wt.% of the Pt-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of Example 7.

This composite catalyst had a relative activity of 4.1 and was evaluated by the method described in Example 7. The catalyst bed contained 8.0 cc of the conventional reforming catalyst of Example 7 in the top of the bed and 12.0 cc of the composite prepared above in this example in the bottom of the bed. The K factor of this catalyst system was 2.9. The temperature of this test was 960°F. The C<sub>8</sub><sup>+</sup> liquid yield at the start of the run was 65 volume%. The C<sub>3</sub><sup>+</sup> yield was 94 volume%. The average octane decline for this test was 0.53 octanes per day which is less than the decline for the conventional Pt-Re of Example 7. The decline in aging rate compared to the standard reforming catalyst of Example 7 was 29%.

**Example 13**

The composite catalyst of this example was prepared by intimate combination of one wt.% of zeolite HZSM35 and 99 wt.% of the commercial Pt-Re reforming catalyst of Example 7.

**Example 14**

A composite of 0.344 g. of the HZSM-35 and 30.7 g of the conventional reforming catalyst of Example 7, which was previously powdered by ball-milling 24 hours, was mixed 2 minutes in a CRC mill, then pelleted and sized 14x25 mesh. This final composite had a relative activity of 2.0 and was evaluated by the method described in Example 7 with the exception that at the run temperature of 930°F the octane at the beginning of the test was only 97.2. The catalyst bed contained 8.0 cc of the Pt-Re on alumina of Example 7 in the top of the bed and 12.0 cc of the composite of this example in the bottom of the bed. The K factor for this sytem was 1.6. The average octane decline for this test was 0.70 octanes per day. This represents a 6% decrease in aging rate compared to the standard reforming

catalyst of Example 7. The  $C_8^+$  liquid yield at the start of the run was 75 volume%. The  $C_3^+$  yield was 93 volume%.

The composite catalyst of this example was prepared by intimate combination of 3 wt.% of steamed zeolite HZSM-35 and 97 wt.% of the Pt-Re on alumina catalyst of Example 7. The HZSM-35, prepared by the method described in Example 13, was steamed for 20 hours at 1100°F in 100% steam atmosphere before compositing with the powdered conventional reforming catalyst of Example 7. This powder mixture was mixed in a CRC mill for 2 minutes and then pelleted and sized 14 to 25 mesh.

The composite had a relative activity of 0.6 and was evaluated by the method described in Ex. 7. The catalyst bed contained 8.0 cc of the Pt-Re/alumina of Ex. 6 in the top of the bed and 12.0 cc of the composite of this example in the bottom of the bed. The K factor for this system was 0.8. The temperature of this test was 950°F. The  $C_8^+$  liquid yield at the start of the runs was 74 volume%. The  $C_3^+$  yield was 90 volume %. The average octane decline for this test was 0.77 octanes per day. Therefore the catalyst system of this example shows no added stability over the commercial Pt-Re catalyst of Example 7.

#### Example 15

The composite of this example was prepared by mixing 0.25 wt.% of an acid (TEA) mordenite with 99.75 wt.% of powdered Pt-Re catalyst of Example 7. The acid TEA mordenite was prepared by the method in Example 12 except the calcined zeolite was not subjected to steaming. The composite was pelleted and sized to 14 to 25 mesh particles.

This composite had a relative activity of 1.3 and was evaluated by the method described in Example 7. The catalyst bed contained 8.0 cc of the conventional reforming catalyst of Example 7 in the top of the bed and 12.0 cc of the composite of this example in the bottom of the bed. The K factor for this system was 1.2. The temperature of the test was 930°F. The  $C_8^+$  liquid yield at the start of the run was 72 volume%. The  $C_3^+$  yield was 95 volume%. The average octane decline for this test was 0.74 octanes per day. The small amount of zeolite in this catalyst failed to stabilize this catalyst system.

#### Example 16

The composite of this example was prepared by compositing 1.15 g (2%) of acid mordenite with 49.15 g. (98%) of the commercial Pt-Re/alumina of Example 7. The mordenite with a silica to alumina ratio of 10 was a commercial sample designated Zeolon H Type 100. The conventional Pt-Re/alumina of Example 7 had been previously ball-milled for 24 hours. The above composite was ball-milled for 2 hours and then pelleted and sized 14x25 mesh. This composite catalyst had a relative activity of 0.8 and was evaluated by the method described in Example 7. The catalyst bed contained 8.0 cc of the Pt-Re standard of Example 7 in the top of the bed and 12.0 cc of the composite of this example in the bottom of the bed. The K factor of this catalyst system was 0.9. The temperature of the test was 960°F. The  $C_8^+$  liquid yield at the start of the run was 73 volume%. The  $C_3^+$  yield was 91 volume%. The average octane decline for this test was .88 octanes per day which is more than the .75 O/D for the commercial Pt-Re catalyst of Example 7.

The HZSM-5 composite of Example 8 (47.5 g) was placed in the fourth reactor of an experimental adiabatic reforming unit having four reactors connected in sequence. The K factor of this system was 3.0. The standard platinum-rhenium-gamma alumina of Example 7 as described hereinabove, was placed in the first, second and third reactors (Case 1).

Table 10

| Reactor | Composite                                    | Relative Activity | Case 1 Vol. (cc) | Case 2 Vol. (cc) |
|---------|----------------------------------------------|-------------------|------------------|------------------|
| 1       | Pt/Re- $Al_2O_3$<br>Catalyst of<br>Example 6 | 1.0               | 19.7             | 19.7             |
| 2       | Pt/Re- $Al_2O_3$                             | 1.0               | 24.6             | 24.6             |
| 3       | Pt/Re- $Al_2O_3$                             | 1.0               | 34.5             | 34.5             |
| 4       | HZSM-5/Pt/Re<br>— $Al_2O_3$                  | 6.4               | 47.5             | —                |
| 4       | Pt/Re- $Al_2O_3$                             | 1.0               | —                | 47.5             |

A comparable run was made with all four reactors loaded with the commercial Pt/Re- $Al_2O_3$  of Example 6 (Case 2).

The start-up for both cases was identical. The catalyst was heated for two hours at 900°F and 200 psig with a fresh hydrogen addition rate of 1—2 cubic feet per hour at a recycle rate of 10.24 cubic feet per hour. The temperature was dropped to 700°F, fresh hydrogen addition discontinued and 2.5 cu. ft/hr of hydrogen containing 400 ppm of hydrogen sulfide was fed to the unit with a recycle rate

of 8.3 cu. ft/hour. When additional  $H_2S$  was no longer consumed by the catalyst,  $H_2S$  addition was stopped and fresh hydrogen added until a recycle flow rate of 10.24 cu. ft/hr was established.

A liquid charge stock having the properties shown in Table 11 was pumped into the unit at 185 ml/hr. The temperature was increased to 800°F. During a 4 hour period chlorine (0.18 wt.% of catalyst) as tertiary butyl chloride was pumped into the unit in the charge stock. During the remainder of the run chloride was continuously added at the rate of 0.046 g (as tertiary butyl chloride) per 100 g. of catalyst per day.

**Table 11**  
**Charge stock:  $C_8$ -370°F Paraffinic Naphtha**

|    |                   |        |    |
|----|-------------------|--------|----|
| 10 | <i>Properties</i> |        | 10 |
|    | PONA, wt.%        |        |    |
|    | P                 | 59.0   |    |
|    | N                 | 28.1   |    |
|    | A                 | 12.9   |    |
| 15 | Specific Gravity  | 0.7411 | 15 |
|    | ASTM, °F          |        |    |
|    | 10%               | 204    |    |
|    | 30%               | 231    |    |
| 20 | 50%               | 257    | 20 |
|    | 70%               | 289    |    |
|    | 90%               | 328    |    |
|    | E.P.              | 365    |    |

25 The temperature was held at 800°F until the water concentration in the overhead from the high pressure separator dropped below 130 ppm. The temperature was increased to 875°F and held until the water concentration dropped below 110 ppm. The temperature was further increased to 900°F and was held there for 2 hours. The temperature was then increased to 930°F. The pressure was 200 psig, the space velocity was 1.43 vol. of liquid per vol. of catalyst per hour and the total recycle ratio was 10.4 moles of recycle gas per mole of charge naphtha.

30 During the run in Case 2, where the inlet temperatures to all four reactors were kept equal, the temperatures were appropriately increased up to an end point of 990°F in order to maintain a 100 clear research octane number for the  $C_8^+$  liquid product. The calculated  $C_8^+$  clear research octane number of the material leaving the 3rd and entering the 4th reactors was 98. A temperature increase at the rate of 2.9°F per day was required to maintain this octane number.

35 In Case 1, the inlet temperatures to reactors 1, 2 and 3 were kept equal. The temperatures were appropriately increased to maintain a 95 clear research octane number for the  $C_8^+$  product leaving the 3rd reactor and entering the 4th reactor. This required an increase of 0.4°F per day. The inlet temperature of the 4th reactor at 930°F maintained a 100 clear research octane number for the  $C_8^+$  liquid product from the total unit.

40 The total cycle time for Case 1 far exceeds the cycle time for Case 2. Case 2 reached the end point temperature in 17 days which was 49°F above its start-of-cycle temperature. Case 1 in 35 days showed a 15°F increase for the first, second and third reactors. Reactor 4 remained constant. It is obvious that Case 1 will show far superior cycle life than Case 2. This longer cycle life is the result of the superior activity and stability of HZSM-5 composite in the 4th reactor of Case 1.

#### 45 Claims

1. A reforming process, in which a reforming feed is contacted under reforming conditions with an inventory of a catalyst comprising from 0.01 to 2 per cent by weight of a platinum group metal, from 0.01 to 3 per cent by weight of halogen and a carrier therefore, characterised in that from 1 to 100 per cent volume of the catalyst in said inventory contains from 0.1 to 25 per cent by weight of a crystalline zeolite selected from ZSM-5, ZSM-11, ZSM-35 and tetraethylammonium mordenite and that the K factor (as herein defined) of said inventory is from 1.5 to 15.

2. A process according to claim 1, wherein said catalyst also contains one or more metals not of the platinum group.

3. A process according to claim 1 or claim 2 wherein said catalyst also contains rhenium.

55 4. A process according to any preceding claim wherein said carrier is eta- and/or gamma-alumina.

5. A process according to any preceding claim in which said inventory is disposed in zones one or more of which consists of catalyst which contains zeolite.

60 6. A process according to any preceding claim wherein said inventory occupies at least three catalyst beds in series.



of 8.3 cu. ft/hour. When additional H<sub>2</sub>S was no longer consumed by the catalyst, H<sub>2</sub>S addition was stopped and fresh hydrogen added until a recycle flow rate of 10.24 cu. ft/hr was established.

A liquid charge stock having the properties shown in Table 11 was pumped into the unit at 185 ml/hr. The temperature was increased to 800°F. During a 4 hour period chlorine (0.18 wt.% of catalyst) as tertiary butyl chloride was pumped into the unit in the charge stock. During the remainder of the run chloride was continuously added at the rate of 0.046 g (as tertiary butyl chloride) per 100 g. of catalyst per day.

Table 11  
Charge stock: C<sub>8</sub>-370°F Paraffinic Naphtha

|    |                  |        |    |
|----|------------------|--------|----|
| 10 | Properties       |        | 10 |
|    | PONA, wt.%       |        |    |
|    | P                | 59.0   |    |
|    | N                | 28.1   |    |
|    | A                | 12.9   |    |
| 15 | Specific Gravity | 0.7411 | 15 |
|    | ASTM, °F         |        |    |
|    | 10%              | 204    |    |
|    | 30%              | 231    |    |
| 20 | 50%              | 257    | 20 |
|    | 70%              | 289    |    |
|    | 90%              | 328    |    |
|    | E.P.             | 365    |    |

The temperature was held at 800°F until the water concentration in the overhead from the high pressure separator dropped below 130 ppm. The temperature was increased to 875°F and held until the water concentration dropped below 110 ppm. The temperature was further increased to 900°F and was held there for 2 hours. The temperature was then increased to 930°F. The pressure was 200 psig, the space velocity was 1.43 vol. of liquid per vol. of catalyst per hour and the total recycle ratio was 10.4 moles of recycle gas per mole of charge naphtha.

During the run in Case 2, where the inlet temperatures to all four reactors were kept equal, the temperatures were appropriately increased up to an end point of 990°F in order to maintain a 100 clear research octane number for the C<sub>8</sub><sup>+</sup> liquid product. The calculated C<sub>8</sub><sup>+</sup> clear research octane number of the material leaving the 3rd and entering the 4th reactors was 98. A temperature increase at the rate of 2.9°F per day was required to maintain this octane number.

In Case 1, the inlet temperatures to reactors 1, 2 and 3 were kept equal. The temperatures were appropriately increased to maintain a 95 clear research octane number for the C<sub>8</sub><sup>+</sup> product leaving the 3rd reactor and entering the 4th reactor. This required an increase of 0.4°F per day. The inlet temperature of the 4th reactor at 930°F maintained a 100 clear research octane number for the C<sub>8</sub><sup>+</sup> liquid product from the total unit.

The total cycle time for Case 1 far exceeds the cycle time for Case 2. Case 2 reached the end point temperature in 17 days which was 49°F above its start-of-cycle temperature. Case 1 in 35 days showed a 15°F increase for the first, second and third reactors. Reactor 4 remained constant. It is obvious that Case 1 will show far superior cycle life than Case 2. This longer cycle life is the result of the superior activity and stability of HZSM-5 composite in the 4th reactor of Case 1.

#### 45 Claims

1. A reforming process, in which a reforming feed is contacted under reforming conditions with an inventory of a catalyst comprising from 0.01 to 2 per cent by weight of a platinum group metal, from 0.01 to 3 per cent by weight of halogen and a carrier therefore, characterised in that from 1 to 100 per cent volume of the catalyst in said inventory contains from 0.1 to 25 per cent by weight of a crystalline zeolite selected from ZSM-5, ZSM-11, ZSM-35 and tetraethylammonium mordenite and that the K factor (as herein defined) of said inventory is from 1.5 to 15.

2. A process according to claim 1, wherein said catalyst also contains one or more metals not of the platinum group.

3. A process according to claim 1 or claim 2 wherein said catalyst also contains rhenium.

4. A process according to any preceding claim wherein said carrier is eta- and/or gamma-alumina.

5. A process according to any preceding claim in which said inventory is disposed in zones one or more of which consists of catalyst which contains zeolite.

6. A process according to any preceding claim wherein said inventory occupies at least three catalyst beds in series.

7. A process according to claim 6 wherein the first bed consists of zeolite-containing catalyst and the remaining beds consist of catalyst not containing a zeolite.
8. A process according to claim 6 wherein the last bed consists of zeolite-containing catalyst and the remaining beds consist of catalyst not containing a zeolite.
- 5 9. A process according to any preceding claim wherein the K factor is from 1.5 to 10. 5
- 10 10. A process according to any preceding claim wherein the K factor is 2 to 5. 10
11. A process according to any preceding claim in which the zeolite has been steamed.
12. A process according to any preceding claim in which the particle size of the zeolite is more than 10 microns.
- 10 13. A reforming catalyst system in which the total catalyst comprises from 1 to 100 per cent of a composite comprising: 10
- (a) an effective amount, up to 25 per cent by weight of a crystalline zeolite selected from ZSM-5, ZSM-11, ZSM-35, and tetraethylammonium mordenite,
- (b) not less than 75 per cent, by weight, of a carrier material,
- 15 (c) from 0.01 per cent to 2 per cent by weight of a platinum group metal either alone or in combination with other metals, and 15
- (d) from 0.01 to 3 per cent by weight of a halide and from 0 per cent to 99 per cent of a conventional reforming catalyst composition comprising:
- [a] a carrier material,
- 20 [b] from 0.01 per cent to 2 per cent by weight of a platinum group metal either alone or in combination with other metals, and 20
- [c] from 0.01 per cent to 3 per cent by weight of a halide
- said total catalyst system having a K factor from 1.5 to 15, this factor being as defined in Equations 2 and 3 herein.
- 25 14. A reforming process according to claim 1 substantially as described in the foregoing Examples. 25

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\* C L M S \*