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3,159,588

## SILICA-ZIRCONIA-TITANIA HYDROCRACKING CATALYST

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This invention relates to methods for the catalytic hydrocracking of high boiling hydrocarbon oils to produce therefrom lower boiling fractions such as gasoline. More particularly the invention concerns the use of certain novel catalysts for the hydrocracking, said catalysts being composed substantially exclusively of silica, zirconia, and titania.

It is a principal object of this invention to provide efficient and selective catalysts for the hydrocracking of mineral oils, which will effect a maximum conversion to high quality gasoline-boiling range hydrocarbons, and a minimum of destructive degradation to products such as methane and coke. Another object is to provide active catalysts which are also thermally stable, and hence may be utilized for long periods of time, and may be regenerated by combustion when the activity declines. Another object is to provide optimum process conditions for the utilization of such catalysts. A further object is to provide hydrocracking catalysts which are more economical than previously utilized catalysts. A still further object is to provide methods for effectively desulfurizing and denitrogenating high boiling feed stocks. A specific object is to provide catalysts which are effective for the hydrocracking of such highly refractory stocks as cycle oils from conventional thermal or catalytic cracking, whereby additional conversion to gasoline may be obtained. Still another object is to provide effective promoters for increasing the intrinsic activity of silica-zirconia-titania hydrocracking catalysts, and prolonging the active life thereof between regenerations. Other objects and advantages will be apparent from the description which follows.

It is well known that the cracking of petroleum stocks, such as virgin gas oils from any type of crude oil, invariably leads to the production of a considerable proportion of a fraction which boils in the same range as the initial charge stocks, but which is much more refractory toward further cracking. This is true whether the cracking process is noncatalytic or catalytic, and as a result there are definite limitations on the degree to which profitable recycling of this fraction to the cracking operation can be practiced. The effect of increased refractoriness of the "unconverted" portion of a cracking stock is particularly limiting in the case of catalytic cracking, so much so that only small recycle ratios are generally employed, further conversion of the recycle stock often being effected in a subsequent thermal cracking operation. Recycling to extinction invariably results in poor selectivity of the conversion to gasoline as a result of excessive formation of carbonaceous catalyst deposits and of light hydrocarbon gases. This is also true in thermal cracking, except that, instead of carbonaceous catalyst deposits, a large amount of heavy tar of high carbon content is formed.

The refractoriness of cracked recycle stocks is the result, principally, of the formation of polynuclear aromatic hydrocarbons through reactions of dehydrogenation, hydrogen transfer, cracking, cyclization, or condensation. It is well known, for example, that recycle stocks from catalytic cracking have a high content of methylnaphthalenes. These may be formed by the cracking of long side-chains or of saturated rings attached to a naphthalene nucleus, by the dehydrogenation of polynuclear

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naphthenes or aromatic-naphthenes such as alkyltetralins, and even by the polymerization and cyclization of olefins produced from saturated hydrocarbons or alkyl side-chains. In thermal cracking, one important mechanism of polynuclear aromatic hydrocarbon formation is the condensation of diolefins with aromatics of lower ring content.

In catalytic cracking, another important factor leading to apparent refractoriness is the accumulation of pyridine- or quinoline-type compounds and carbazoles in the recycle stock. These basic nitrogen compounds exert a temporary poisoning effect on the acidic catalyst centers, and low conversion of the cycle stock results.

The above-noted difficulties are avoided or minimized by the process herein described. Thus, by preventing complete dehydrogenation of polynuclear naphthenes to polynuclear aromatics, by hydrogenating at least partially the polynuclear aromatics already present in the charge stock, by preventing high olefin or diolefin content with subsequent reactions of polymerization, cyclization, or condensation, and by decomposing basic nitrogen compounds to ammonia, relatively high partial pressures of hydrogen can permit a maximum theoretical conversion of heavy hydrocarbons of all types to hydrocarbons boiling in the desired gasoline range. A process which, in a single step, employs sufficient hydrogen to cause an appreciably greater conversion of any higher boiling hydrocarbon mixture to gasoline than is possible in one step by conventional catalytic or noncatalytic cracking processes is termed "hydrocracking" for the purposes of this description of invention. In all cases such a process will depend on the use of a suitable catalyst which not only promotes cracking but also activates molecular hydrogen to such an extent that hydrogen will enter into the cracking at some stage, presumably in the very initial stages.

From the above discussion it will be apparent that the catalysts of the present invention may be used advantageously in the hydrocracking of virgin gas oils, whereby greater conversion to gasoline is obtained in a once-through operation than would be obtained in a similar once-through operation in conventional cracking processes, and also the "unconverted" fraction is not degraded with respect to refractoriness, and may hence be recycled substantially to extinction. It will be apparent also that the catalyst may be employed to treat the refractory residues from conventional cracking operations whereby a substantial yield of high quality gasoline is obtained. The residue from this operation may likewise be recycled either to the hydrocracking step or back to a conventional cracking step in the absence of hydrogen. These results are not obtainable when treating such recycle stocks with a conventional silica-alumina catalyst; hydrogen is practically without effect on the cracking of such stocks with this catalyst.

The hydrocracking conditions employed herein involve passing the vaporized hydrocarbons over the finished catalyst at temperatures ranging between about 500° and 950° F. (preferably between 600° and 850° F.), hydrogen pressures above about 100 p.s.i.g., preferably between about 500 and 5000 p.s.i.g., and space velocities ranging between about 0.1 and 10.0. The preferred hydrogen ratios may range between about 1000 and 10,000 s.c.f. per barrel of feed. The minimum hydrogen pressure of about 500 p.s.i.g. is critical herein when treating highly refractory, aromatic cycle stocks; at lower pressures dehydrogenation is favored, resulting in increased aromaticity and refractoriness of the stock. The optimum conditions herein defined are adapted to effect partial hydrogenation of fused-ring aromatic hydrocarbons to more highly saturated ring compounds, which are in turn more readily cracked to produce ultimately, monocyclic aromatic hydrocarbons and low-boiling paraffins.

The basic active component of the catalysts employed herein consists of the silica-zirconia-titania composite, herein referred to as the hydrocracking "base." This base, more particularly described hereinafter, is not to be confused with conventional catalyst carriers, whose function is merely to provide an extended surface area for the deposition of other active ingredients. I have recently shown that the silica-zirconia-titania composites in themselves possess excellent intrinsic hydrocracking activity. None of the three ingredients thereof singly, or any combination thereof, had been previously known to possess hydrocracking activity, and only the silica-zirconia combination had been known to possess cracking activity, and this only in the absence of hydrogen. It hence came as a distinct surprise to find that the silica-zirconia-titania composite was an active hydrocracking catalyst, and was more active than silica-zirconia, and at least as active as silica-titania while being considerably more heat-stable.

The term "heat-stable" as employed herein refers to the resistance of the active, amorphous compositions toward the formation of definite crystalline phases under the influence of prolonged heating and/or high temperatures. The formation of such crystalline phases has been found to parallel roughly the decline in intrinsic activity of the catalysts, i.e., the decline which is not attributable to extrinsic factors such as fouling with coke or other poisons. The term "activity" refer to the ability of the catalyst to promote the formation of gasoline from higher boiling materials under the described hydrocracking conditions. This "activity" factor has two counterparts: over-all ability to promote the hydrogenative scission of hydrocarbons under hydrogen pressure, and specific selectivity for promoting the formation of gasoline in preference to undesired materials such as coke, methane, ethane, propane and the like.

The base compositions found to be most useful for hydrocracking comprise those which contain between about 5% and 75% of silica, between about 5% and 75% zirconia, and between about 5% and 75% of titania, all proportions being by weight on a dry basis. The preferred bases are those wherein zirconia and titania comprise the major portion thereof, silica being the minor component. The high-silica compositions are generally quite heat stable, but those containing more than about 65% by weight of silica are in general much less active than those containing lesser proportions. The bases containing less than about 10% of silica may be initially quite active, but are not sufficiently heat-stable for most practical purposes. The optimum proportions of ingredients are roughly equi-molar; i.e., the equimolar compositions appear to exhibit the optimum combination of activity, selectivity, and heat stability. The mole-ratio of  $ZrO_2/TiO_2$  is preferably between about 0.2 and 2.0. The highest activity is exhibited by those compositions containing more than 15% of titania, and more than 15% of zirconia in the base. The greatest heat stability is exhibited by those base compositions which contain less than about 65% of titania. For all these reasons the preferred base compositions embrace those falling within the following ranges.

| Component:     | Optimum wt. percent |
|----------------|---------------------|
| Silica -----   | 10-65               |
| Titania -----  | 15-65               |
| Zirconia ----- | 15-65               |

In the preparation of active silica-zirconia-titania catalysts it is essential that the three components be extremely intimately mixed, such as is achieved by coprecipitation of  $SiO_2$ ,  $TiO_2$  and  $ZrO_2$ . Such catalysts may be prepared by any method which provides a sufficiently intimate association of the components. Molecular subdivision and distribution of the components in an amorphous, activated gel structure is preferred. Suitable methods for obtaining such composites includes for example: (1) the

impregnation of a hydrogel or adsorbent gel of one component, or of a mixture of two components, with a solution or hydrosol of the other component or components, followed by drying and calcining; (2) coprecipitation of all three components from a solution or solutions of soluble compounds thereof, followed by drying and calcining; (3) coprecipitation of two of the components from a solution or solutions of soluble compounds thereof, followed by impregnation of the two-component gel with the third component, followed by drying and calcining. Any other method may be employed which provides a sufficiently intimate association of the components. It is to be noted that the methods employing impregnation (methods 1 and 3) are feasible only where the materials added by impregnation are to make up a minor portion, e.g., 5-20% by weight of the finished catalyst.

One method of effecting coprecipitation involves forming an aqueous solution of acidic compounds of all three components, e.g., fluosilicic acid, zirconyl chloride, and titanium tetrachloride, and mixing this solution with a suitable alkali such as ammonium hydroxide, thereby to effect a precipitation of the hydrous oxides of silica, titania and zirconia. The precipitate is then removed by filtration, washed exhaustively to remove contaminating ions, dried and calcined.

Another and preferred coprecipitation process may be carried out by forming an aqueous solution of sodium silicate containing excess alkali such as ammonium hydroxide, and mixing the alkaline silicate with a second solution of soluble, acidic titanium and zirconium salts, e.g., zirconium sulfate and titanium sulfate.

Any suitable soluble salts or hydrosols of silica, zirconium and titanium may be employed in the above or other coprecipitation methods described herein. The general objective is to obtain an intimate mixture of the hydrous oxides, or of insoluble compounds which may be transformed to the oxides upon calcining. Suitable materials for preparing coprecipitated composites include for example zirconyl chloride, zirconyl bromide, zirconyl iodide, zirconium sulfate, zirconium acetate, titanium tetrafluoride, titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, titanium sulfate (e.g.,



titanium oxalate, sodium silicate, potassium silicate, fluosilicic acid, silica hydrosols, and the like. The zirconyl halides listed above may be formed in situ by adding to water the corresponding tetra-halide of zirconium.

In one modification, a mixture of crude silica, titania (rutile or anatase), and zirconia may be digested with hydrofluoric acid until all three components are dissolved, and the resulting solution then neutralized with alkali, thereby precipitating the mixed hydrogels. In another modification mixtures of crude titania and zirconia may be digested with acids, e.g., sulfuric or hydrofluoric, until dissolved, and the resulting solution mixed rapidly with a sodium silicate solution containing sufficient excess alkali to neutralize the free acid, thereby precipitating hydrous silica, titania and zirconia.

It should be noted that all three of the hydrous oxides are generally precipitable over the pH range from about 3 to 12.

The coprecipitated gels prepared by any of the above methods are recovered as by filtration or the like, washed exhaustively, dried and calcined at e.g., 500-1500° F. for 1 to 24 hours to form a xerogel. If the hydrous gels are contaminated with alkali metals, it is preferable to leach with ammonium sulfate, ammonium nitrate or ammonium chloride solutions to replace the alkali metal ion with ammonium ion which is decomposed to hydrogen ion during calcining.

An important consideration in preparing the coprecipitated gels involves the hydrogen ion concentration of the aqueous medium in and surrounding the immediate zone of precipitation. It has been found that when alkaline

sodium silicate solutions are stirred gradually into a large volume of acidic titanium and zirconium compounds, whereby the precipitation occurs in a prevailing acidic environment, the resulting catalysts are generally much less active than those prepared by gradually stirring the acid salt solutions into a large volume of alkaline silicate. In the latter case, the precipitation occurs in an environment which is prevailing alkaline. It is therefore preferred that the coprecipitation be carried out under conditions such that the prevailing environment is one of alkalinity, i.e., at a pH between about 6 and 12. Repeated experiments have demonstrated that the base catalysts prepared by coprecipitating in acid environment, i.e., at a pH between about 2 and 6, are initially substantially less active than catalysts of the same nominal composition precipitated from alkaline solutions. The most practical method presently contemplated for obtaining controlled alkaline precipitation involves the simultaneous mixing in a small surge zone of a stream of acidic solution of zirconium and titanium salts with a stream of alkaline silicate solution containing sufficient excess alkali to neutralize the acid salt solution. The flow rates of the respective streams are controlled so as to provide a substantially constant pH in the mixing zone. However, any other practical method may be utilized which effectively maintains the precipitating environment under prevailing alkaline conditions during precipitation.

While the effect of pH during precipitation is not completely understood, it is found that the bases prepared under alkaline conditions exhibit a substantially higher surface area and pore volume than those prepared under acid conditions, which factors would appear to account in large part for their improved activity. Thus, in one series of preparations by coprecipitation, the following surface area and pore volume characteristics of the pelleted catalysts were found:

TABLE 1

| Catalyst | Composition, Wt. Percent |                  |                  | pH of pptn. | Surface Area, M <sup>2</sup> /gm. | Pore Volume, ml./gm. |
|----------|--------------------------|------------------|------------------|-------------|-----------------------------------|----------------------|
|          | SiO <sub>2</sub>         | ZrO <sub>2</sub> | TiO <sub>2</sub> |             |                                   |                      |
| A-----   | 23                       | 47               | 30               | 5.0         | 111                               | 0.306                |
| B-----   | 23                       | 47               | 30               | 8.5         | 191                               | 0.481                |
| C-----   | 50                       | 20               | 30               | 5.0         | 189                               | 0.295                |
| D-----   | 50                       | 20               | 30               | 8.5         | 200                               | 0.468                |

Catalysts B and D exhibit a substantially greater hydrocracking activity than catalysts A and C, respectively. It is therefore preferred to utilize the catalyst bases having a pore volume in excess of about 0.3 ml. per gm. of catalyst pellet. When the respective bases are impregnated with a promoter, the final catalysts prepared from the alkaline coprecipitated bases also display higher surface areas and pore volumes than those prepared from the acid precipitated bases.

It has been found also that the coprecipitated bases prepared from the sulfate salts of zirconium and titanium are somewhat more active and stable than the compositions prepared from the halide salts. It is therefore preferred to utilize the soluble sulfates of zirconium and titanium.

Suitable alkalis to be used in coprecipitation comprise for example ammonia, sodium hydroxide, potassium hydroxide, lithium hydroxide, or in general any of the alkali metal or ammonium hydroxides, carbonates, bicarbonates, sulfides or hydrosulfides. Organic bases such as methylamine, dimethylamine, trimethylamine, tetramethyl ammonium hydroxide, hexamethylene tetramine and the like may also be used.

In any of the above preparation methods, the catalyst may be formed into pellets or granules at various stages in the manufacture. The moist powders may be compressed or extruded to form pellets prior to calcining, or the calcined, powdered gels may be compressed to form the desired pellets. Ordinarily it is desirable to employ the catalyst in the form of pellets or granules ranging in size

from about 1/8 inch to 1/2 inch in diameter. In forming such pellets it may be desirable to employ minor proportions of binders such as hydrogenated corn oil or the like, and in case the dry materials are to be pelleted, a small proportion, e.g., 1-2% by weight, of graphite may be incorporated therein to act as a lubricant. The binders and lubricants, if employed, are removed by combustion during the final calcining. Those skilled in the art will readily appreciate that other compounding and pelleting procedures may be employed.

The above catalysts may be utilized for hydrocracking a great variety of mineral oil feed stocks, which are generally high boiling fractions derived from petroleum stocks, shale oils or tar sands. The catalysts are especially useful for hydrocracking coker gas oils, refractory cycle stocks from conventional cracking operations, or alternatively they may be used for hydrocracking virgin gas oils to prevent the buildup of refractory residues from the cracking operation. Any of these feed stocks may also contain organic sulfur in amounts up to about 4% by weight, and organic nitrogen in amounts up to about 2% by weight. In the hydrocracking process these sulfur and nitrogen compounds are largely decomposed.

After long periods of use, the catalysts may decline in activity to an undesirable level as a result of coke deposits and other inactivating factors associated with the hydrocracking process. When this occurs, the catalysts may be restored substantially to their initial activity by oxidative regeneration, as by heating in the presence of air, or air-flue gas mixtures at 350°-800° C. for 3 to 48 hours.

The following examples are cited to illustrate the effectiveness of the herein described catalysts for hydrocracking, but such examples should not be construed as limiting in scope:

#### Example I

A series of coprecipitated base catalysts, each containing silica and one or more of the components zirconia, and titania was prepared by neutralizing ammoniacal sodium silicate solutions with appropriate proportions of acidic solutions containing varying proportions of zirconium sulfate ( $Zr(SO_4)_2 \cdot 4H_2O$ ), or titanium tetrachloride, or both. The overall proportions of the salts utilized were such as to give the desired ratio of silica, zirconia, and/or titania in the finished catalyst. The method of precipitating involved adding the acidic zirconium and/or titanium solution gradually with stirring to the ammoniacal sodium silicate solution containing sufficient ammonia exactly to neutralize the acidic salt solution when completely added. The resulting coprecipitation occurred at a pH ranging from about 12 to 6. Other catalysts were prepared by the reverse order of addition with results as indicated below.

The mixed hydrogels from the above coprecipitations were filtered from the solutions, partially dried, washed with an aqueous ammonium sulfate solution to remove zeolitic sodium, washed with water until free of sulfate, dried, pulverized and formed into 1/8" pellets. The pellets were then calcined at 900° F. for 18 hours.

Pure zirconia and titania gels were prepared by precipitation with ammonia from aqueous solutions of zirconyl chloride or titanium tetrachloride, followed by washing, drying and calcining.

The catalysts prepared as outlined were then tested for hydrocracking activity employing a refractory cycle stock from a commercial catalytic cracking operation, representing a relatively difficult stock for conversion to gasoline by conventional catalytic cracking processes. This stock had the following characteristics:

|                                               |         |      |
|-----------------------------------------------|---------|------|
| API gravity at 60° F. -----                   | degrees | 21.3 |
| ASTM distillation end point -----             | ° F.    | 673  |
| Vol. percent 400° F. end-point gasoline ----- |         | 2.1  |
| Wt. percent sulfur -----                      |         | 0.92 |
| Wt. percent nitrogen -----                    |         | 0.14 |
| Vol. percent aromatics -----                  |         | 62   |

|                                                     |      |
|-----------------------------------------------------|------|
| Vol. percent olefins -----                          | 5    |
| Vol. percent saturates -----                        | 33   |
| The processing conditions employed were as follows: |      |
| Temperature ----- ° F                               | 900  |
| Pressure ----- p.s.i.g.                             | 1000 |
| LHSV -----                                          | 0.5  |
| H <sub>2</sub> /liquid feed ----- s.c.f./bbl        | 8000 |
| Length of runs ----- hours                          | 6    |

The results of the various runs were as follows:

TABLE 2

| Catalyst |                             |                  |                  | Gasoline Yield,<br>Vol. percent of feed |                   | Average<br>Selectivity <sup>3</sup> |
|----------|-----------------------------|------------------|------------------|-----------------------------------------|-------------------|-------------------------------------|
| No.      | Composition,<br>Wt. percent |                  |                  | Avg. <sup>1</sup>                       | Max. <sup>2</sup> |                                     |
|          | SiO <sub>2</sub>            | ZrO <sub>2</sub> | TiO <sub>2</sub> |                                         |                   |                                     |
| 1        | 0                           | 100              | 0                | 19                                      | 21                | 64                                  |
| 2        | 10                          | 90               | 0                | 35                                      | 36                | 77                                  |
| 3        | 20                          | 80               | 0                | 37                                      | 39                | 67                                  |
| 4        | 20                          | 80               | 0                | 40                                      | 51                | 76                                  |
| 5        | 20                          | 70               | 10               | 28                                      | 28                | 95                                  |
| 6        | 20                          | 70               | 10               | 41                                      | 48                | 83                                  |
| 7        | 20                          | 60               | 20               | 55                                      | 72                | 80                                  |
| 8        | 20                          | 50               | 30               | 59                                      | 74                | 85                                  |
| 9        | 20                          | 40               | 40               | 53                                      | 74                | 68                                  |
| 10       | 20                          | 30               | 50               | 49                                      | 70                | 76                                  |
| 11       | 20                          | 20               | 60               | 67                                      | 71                | 81                                  |
| 12       | 20                          | 10               | 70               | 37                                      | 61                | 57                                  |
| 13       | 20                          | 0                | 80               | 59                                      | 76                | 78                                  |
| 14       | 10                          | 0                | 90               | 54                                      | 65                | 78                                  |
| 15       | 0                           | 0                | 100              | 25                                      | 34                | 80                                  |
| 16       | 50                          | 30               | 20               | 43                                      | 56                | 77                                  |

<sup>1</sup> Average for full six hour run.

<sup>2</sup> Product from first hour of run.

<sup>3</sup> Selectivity =  $\frac{\text{Vol. percent gasoline yield}}{100 - \text{Vol. percent liquid residue}} \times 100$ .

<sup>4</sup> Catalysts coprecipitated over pH range from about 0 to 7; others coprecipitated over range from about 12 to 6.

Catalysts No. 13 and 14, while initially quite active, are definitely inferior to the three-component catalysts 6 to 11 in terms of thermal stability. Catalysts 6 to 11 showed by differential thermal analysis, major transition points in the temperature range of 1324° to 1530° F., while No. 13 showed a major transition point at only 1121° F., and No. 14 showed no distinct transition point, crystallization occurring evenly over a broad temperature range. The addition of zirconia hence provides a definite improvement in thermal stability.

In addition to the data reported in Table 1, it was found that the products from the hydrocracking runs were substantially desulfurized and denitrogenated. For the preferred catalysts 6 through 12, it was found that desulfurization was from 69% to 96% complete, and denitrogenation was from 75% to 98% complete.

### Example II

This example demonstrates the critical range of SiO<sub>2</sub> content in the catalyst.

A series of catalysts of varying SiO<sub>2</sub> ratio, but substantially constant ZrO<sub>2</sub>/TiO<sub>2</sub> ratio, were prepared and tested for hydrocracking a mixture of light catalytic cracking cycle oils, the mixture having a gravity of 23.7° API, an end point of 657° F. and an acid-solubles content of 58%. The hydrocracking conditions were:

|                                      |      |
|--------------------------------------|------|
| Temperature ----- ° F                | 850  |
| Pressure ----- p.s.i.g.              | 3000 |
| LHSV -----                           | 2.0  |
| H <sub>2</sub> /oil ----- s.c.f./bbl | 8000 |

The results were as follows:

TABLE 3

| No.      | Composition, Wt. Percent                                                    | Hours on Stream | Vol. Percent Conversion | Percent C <sub>4</sub> + Gasoline <sup>b</sup> | Research Octane No. |            |
|----------|-----------------------------------------------------------------------------|-----------------|-------------------------|------------------------------------------------|---------------------|------------|
|          |                                                                             |                 |                         |                                                | Clear               | +3 ml. TEL |
| 28.----- | 20 SiO <sub>2</sub> -50ZrO <sub>2</sub> -30TiO <sub>2</sub> -----           | 20              | 49.4                    | 56.5                                           | 83.4                | 94.6       |
| 29.----- | 30 SiO <sub>2</sub> -42ZrO <sub>2</sub> -28TiO <sub>2</sub> -----           | 26              | 40.7                    | 46.7                                           | 85.6                | 90.3       |
| 30.----- | 50 SiO <sub>2</sub> -30ZrO <sub>2</sub> -20TiO <sub>2</sub> -----           | 18              | 29.7                    | 32.6                                           | 85.3                | 94.6       |
| 31.----- | 75 SiO <sub>2</sub> -15ZrO <sub>2</sub> -10TiO <sub>2</sub> -----           | 23              | 16.5                    | 17.6                                           | 84.7                | 93.9       |
| 32.----- | (20 SiO <sub>2</sub> -50ZrO <sub>2</sub> -30TiO <sub>2</sub> ) 1.2 Ni.----- | 18              | 54.3                    | 63.1                                           | 83.0                | 94.6       |
| 33.----- | (30 SiO <sub>2</sub> -42ZrO <sub>2</sub> -28TiO <sub>2</sub> ) 1.0 Ni.----- | 28              | 58.0                    | 69.4                                           | 84.7                | 96.8       |
| 34.----- | (50 SiO <sub>2</sub> -30ZrO <sub>2</sub> -20TiO <sub>2</sub> ) 1.0 Ni.----- | 20              | 52.7                    | 60.5                                           | 85.3                | 97.3       |
| 35.----- | (75 SiO <sub>2</sub> -15ZrO <sub>2</sub> -10TiO <sub>2</sub> ) 1.1 Ni.----- | 26              | 23.7                    | 25.5                                           | 84.2                | 94.9       |

<sup>a</sup> Catalysts prepared by coprecipitation of SiO<sub>2</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub> from ammoniacal sodium silicate and Zr(SO<sub>4</sub>)<sub>2</sub>-TiOSO<sub>4</sub> solutions. Calcined base impregnated with nickel nitrate and recalcined.

<sup>b</sup> Volume percent of cycle oil feed.

From the foregoing data it will be apparent that the acid solution of zirconium and titanium, are substantially three-component catalysts 5 through 12, and 16, are in general substantially more active than either the single-component or the two-component silica-zirconia catalysts, in terms of average gasoline yields. The selectivity of the three-component catalysts is also in most cases superior to the two-component catalysts. Catalysts 3 and 5, which were coprecipitated in an acid environment by pouring the ammoniacal sodium silicate into the less active than corresponding catalysts 4 and 6 respectively, which were precipitated in an alkaline environment by pouring the acidic zirconium-titanium solution into the ammoniacal sodium silicate. In the case of catalyst 5 however, the high selectivity indicates that under more severe processing conditions the gasoline yield could be increased without unduly impairing the selectivity.

From the above data, it will be apparent that 50% is about the maximum SiO<sub>2</sub> content for the unpromoted catalysts 28-31, if maximum activity is desired. For the promoted catalysts 32-35, a considerably larger proportion of SiO<sub>2</sub> is permissible, ranging up to about 75%, but for acceptable activity about 65% is the top limit.

Catalysts which contain less than about 10% SiO<sub>2</sub> may be initially very active, but soon decline as a result of marked thermal instability.

This application is a continuation-in-part of application Serial No. 698,398, filed November 25, 1957, which in turn is a continuation-in-part of (1) application Serial No. 617,222, filed October 22, 1956, and (2) application Serial No. 539,680, filed October 10, 1955, all of said patent applications now being abandoned.

From the above examples it will be apparent that the catalysts described herein exhibit surprisingly high activity for the hydrocracking of refractory cycle stocks and other heavy oils to produce high yields of high-octane gasoline,

and good desulfurization and denitrogenation of such oils. It is not intended that the invention should be restricted to the details disclosed in the examples or elsewhere, since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A hydrogenating-cracking catalyst consisting essentially of coprecipitated titanium oxide, zirconium oxide and silicon oxide in intimate admixture, the silica content of said catalyst making up a minor proportion greater than 10% thereof, the zirconia content being between about 15% and 65%, and the titania content being between about 15% and 65%, said catalyst having been prepared by coprecipitation of the hydrous gels of titania, zirconia and silica, followed by washing and calcining of the mixed hydrous oxides, said coprecipitation step being carried out by admixing an aqueous alkaline solution with an aqueous acidic solution containing dissolved titanium and zirconium salts selected from the class consisting of halides, sulfates, acetates and oxalates, a soluble silicon compound selected from the class consisting of alkali metal silicates, fluosilicic acid, and silica hydrosols being dissolved in one of said solutions, and controlling said admixing so as to provide an aqueous environment of pH between about 6 and 12 in the immediate zone of coprecipitation.

2. A catalyst as defined in claim 1 wherein said coprecipitation is carried out by gradually pouring said acidic solution of zirconium and titanium salts into a large body of ammoniacal alkali metal silicate solution with agitation, whereby coprecipitation of the hydrous oxides of

silicon, zirconium and titanium takes place at a pH between about 12 and 6.

3. A catalyst as defined in claim 1 wherein soluble sulfates of zirconium and titanium are employed in said coprecipitation step.

4. A catalyst as defined in claim 1 wherein said coprecipitation is carried out by simultaneously admixing a flowing stream of said acidic solution containing dissolved zirconium and titanium salts with a flowing stream of an alkaline, alkali metal silicate solution with agitation, whereby coprecipitation of the hydrous oxides of silicon, zirconium, and titanium takes place at a substantially constant pH between about 6 and 12.

5. A hydrocracking catalyst comprising as essential active ingredients between about 15% and 65% of titania xerogel, between about 15% and 65% of zirconia xerogel, and between about 10% and 65% of silica xerogel, said catalyst having been prepared by coprecipitating the hydrous gels of titania, zirconia and silica from aqueous solution at a pH between about 6 and 12, followed by drying and calcining of the final composition.

6. A catalyst as defined in claim 5 prepared by mixing an aqueous alkali metal silicate solution with an acidic solution containing dissolved zirconium and titanium salts, said zirconium and titanium salts being selected from the class consisting of halides, sulfates, acetates and oxalates.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

|           |          |               |
|-----------|----------|---------------|
| 2,697,066 | Sieg     | Dec. 14, 1954 |
| 2,796,409 | Schwartz | June 18, 1957 |
| 2,911,356 | Hanson   | Nov. 3, 1959  |